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(54) **PROCESSES FOR THE PRODUCTION OF ZINTL COMPOUNDS, INTERMETALLIC COMPOUNDS AND ELECTRONIC COMPONENTS INCLUDING INTERMETALLIC COMPOUNDS**

VERFAHREN ZUR HERSTELLUNG VON ZINTL VERBINDUNGEN, INTERMETALLISCHE VERBINDUNGEN UND ELEKTRONIK BAUTEILE MIT DIESEN INTERMETALLISCHEN VERBINDUNGEN

PROCEDE DE PRODUCTION DE COMPOSES DE ZINTL, ET DE COMPOSES INTERMETALLIQUES, ET COMPOSANTS ELECTRONIQUES INCLUANT LES COMPOSES INTERMETALLIQUES

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Description

[0001] This invention relates to processes for the production of Zintl compounds, processes for the production of intermetallic compounds and processes for manufacturing electronic components including intermetallic compounds. In particular, this invention relates to the application of intermetallic compounds in the manufacture of electronic components. More specifically, this invention relates to a method of applying intermetallic compositions onto the surface of electronic components.

[0002] Intermetallic compounds and Zintl phases have been known for some time. Zintl compounds are binary compounds formed between alkali or alkaline earth elements and post transition elements [(see for example, "Chemistry, Structure, and Bonding of Zintl Phases and Ions", Ed. Susan M. Kauzlarich, VCH Publishers, (1996)]. One of the earliest examples of Zintl ions were those formed by the reaction of sodium in liquid ammonia with a variety of Group 14 metals, such as lead, to form, e.g. $4[Na(NH_3)_n^+][Pb_9]^{4-}$. These complexes are unstable due to the facile liberation of NH_3, which can occur at low temperatures to form intermetallic compositions of the type $NaPb_x$.

[0003] The isolation of solid derivatives of Zintl anions using ethylenediamine in the place of ammonia has been reported in which the alloy composition $NaSn_{2.4\text{-}2.5}$, on slow dissolution in warm ethylenediamine followed by precipitation on the addition of THF or monoglyme, generates the species $Na_4(en)_7Sn_9$ (en = ethylenediamine).

[0004] Macrocyclic ligands, such as 2,2,2-crypt, have been used in place of ammonia or ethylenediamine due to their effective sequestering capabilities. The stability of these cryptate complexes, an example of which includes $[2(2,2,2\text{-crypt-K})^+[Pb_5]^{2+}$, have enabled extensive characterisation of their crystal structures.

[0005] However, hitherto, the available techniques for producing Zintl compounds, have been cumbersome, especially where it is desired to produce Zintl compounds with predetermined stoichiometries. For example, the majority of these compounds have been obtained by dissolving pre-formed stoichiometric alloys of metals in ammonia. This route, which is required to obtain stoichiometric control of the product, involves high-temperature methods and highly specialised techniques. As a result, Zintl compounds, particularly of the heaviest (most metallic) post-transition elements, have generally only been prepared in very small scale (10-50 mg) and have therefore not been broadly accessible to the majority of synthetic chemists or useful in industrial processes.

[0006] As indicated, the invention also relates to processes for producing intermetallic compounds. Intermetallic compounds, which may be defined as mixed metal compounds of the type $M^1_xM^2_y...M^3_z$, possess properties that do not necessarily resemble the respective alloys and often exhibit properties which are intermediate between their component elements.

[0007] The majority of intermetallic alloys behave as semi-conductors and have thus found extensive applications in the electronics industry. Some intermetallic compounds display photoactive properties and these have been employed in photodetector components. The properties of the intermetallic layer are dependent upon the stoichiometry of the metal components. Thus the stoichiometric control of the metal components is important in order to achieve the desired electrical properties of the intermetallic layers.

[0008] The existing process for the manufacture of electronic components such as vacuum photodiodes having intermetallic layers based on antimony and alkali metals, involve the high temperature formation of antimony/alkali metal intermetallic layers using metal vapours. This deposition process typically involves predepositing an antimony layer onto the surface of the electronic component, followed by the addition of an alkali metal in vapour form. This process is highly labour intensive and the characteristics of the intermetallic films deposited are often variable as a consequence of inherently poor control of their stoichiometry.

[0009] It would therefore be highly desirable to improve the method in which intermetallic layers can be deposited onto electronic components during their manufacture. In addition, it would be advantageous to obtain a higher degree of stoichiometric control than those offered by the existing vapour deposition method.

[0010] Thus, it is a further object of the present invention to provide an improved process of forming intermetallic layers for use in the manufacture of electronic components. Such electronic components include photomultipliers and other photodetectors used in, e.g., medical scanners and scientific instruments.

[0011] Another object of the present invention is to provide a method of producing intermetallic layers in which the stoichiometry can be controlled to furnish films with essentially consistent characteristics.

[0012] The present invention in all its aspects followed from the development of a novel procedure for producing Zintl compounds from stable precursors. This procedure enabled for the first time the production of Zintl compounds by a convenient route in a manner which permitted the Zintl compounds to be produced with preselected stoichiometries between the metal components thereof.

[0013] Advantageously, the use of a stable precursor to generate a Zintl compound that may be subsequently converted to an intermetallic alloy according to the present invention, allows the possibility for the deposition of the intermetallic alloy from solution at low temperature. Such a method provides a substantial improvement over existing vapour phase deposition techniques. The method of the present invention provides a convenient route to the formation of Zintl compounds on a gram or multi-gram scale.

[0014] Thus, the invention provides a novel application of Zintl compounds, especially when produced in accordance with the first aspect of the invention, in the manufacture of electronic components having surface coatings formed from intermetallic compounds.

[0015] According to the present invention, there is provided a process for the production of a Zintl compound comprising subjecting a heterometallic phosphinidene complex to thermal decomposition.

[0016] The heterometallic phosphinidene complex typically comprises at least two metals. Preferably one of the metals may be a metal of Group 13, 14 or 15 of the Periodic Table. Particularly preferred metals are those from Group 15 of the Periodic Table, including As, Sb and Bi.

[0017] The second of the metals is preferably a metal of Group 1 of the Periodic Table, e,g, Li, Na, K, Rb or Cs.

[0018] The heterometallic phosphinidene complex used in the process of the invention preferably contains one or more phosphinidene ligands [PR], which may be the same or different. The phosphorus atom of each phosphinidene ligand is covalently linked to a substituted or unsubstituted hydrocarbyl group, R.

[0019] The unsubstituted or substituted hydrocarbyl group, R, typically contains 1 to 15, preferably 4 to 10 carbon atoms, and may be selected from alkyl, alkenyl, alkynyl, cycloalkyl, aryl, aralkyl, and alkaryl. Typical substituents include F and alkylsilyl groups.

[0020] A particularly preferred phosphinidene ligand is PCy (Cy = cyclohexyl, C_6H_{11}), wherein the phosphorus atom is linked to a cyclohexyl group. Other examples of possible substituents include ^tBu [tertiary butyl, $(CH_3)_3C$-], Pr [isopropyl, $(CH_3)_2CH$-], bis(trimethylsilyl) methyl [$(CH_3Si)_2CH$-], tris(trimethylsilyl)methyl {[$(CH_3)_3Si]_3C$-}. trimethylsilyl [$(CH_3)_3Si$] and fluorinated groups such as pentafluorophenyl (C_6F_5).

[0021] The phosphorus atom of each phosphinidene ligand in the heterometallic phosphinidene complex is generally coordinated to four metal atoms. It is preferred that the phosphorus atom is coordinated to three Group I metal atoms and one metal atom of Groups 3, 14 or 15.

[0022] The heterometallic phosphinidene complex may further comprise an additional ligand or ligands which may be Lewis bases. The structure of the complex will depend upon the identities of the metals and ligands.

[0023] Thus the preferred phosphinidene complexes referred to above can have various structures depending on the Group 13, 14 or 15 metal(s) present and on the alkali metal(s) and Lewis base ligand(s). Generally, however, the phosphinidene ligands (PR) are bridged between the Group 13, 14 or 15 metals and the alkali metals (i.e. the complexes will contain M^1-P(R)-M^2 groupings; M^1 = Group 13-15 metal, M^2 = Group 1 metal) and the phosphorus atom of the phosphinidene group will generally be coordinated by up to four metal atoms (for example, one Group 13, 14 or 15 metal and three alkali metals, as in Compound **I**).

[0024] The Group 13, 14 and 15 metals will usually be in their +3, +2 and +3 oxidation states respectively.

[0025] As indicated, the heterometallic phosphinidene complex may further comprise an additional Lewis base ligand coordinated to one or more of the metal atoms. Preferred Lewis base ligands are primary, secondary or tertiary amines of formula $R^1R^2R^3N$, wherein each of R^1, R^2 and R^3 represent hydrogen, a C_1-C_{10} alkyl or C_6-C_{10} aryl group. In addition other Lewis bases such as polyamines [e.g. ethylenediamine $(H_2NCH_2)_2$], permethylated polyamines (for example TMEDA {[$(CH_3)_2NCH_2]_2$} and PMDETA {[$(CH_3)_2NCH_2CH_2]_2NCH_3$}), pyridine ($C_5H_5N$) or polypyridines [such as 2,2'-bipyridine $(C_5H_4N)_2$], may be employed. Oxygen donors such as ethers (e.g. tetrahydrofuran, THF) may also be used.

[0026] The thermal decomposition process of the invention may result in the co-production of a phosphorus compound having at least one P-P bond, e.g. a cyclic phosphinidene. The thermal decomposition typically involves a so-called "reductive phosphinidene coupling" or "reductive elimination" in the conversion of the phosphinidene intermediate into the Zintl complex. In such instances, the formation of phosphorus-phosphorus bonds, which have the highest bond energy between any Group 15 elements, provides the necessary thermodynamic driving force for the reaction to take place. As indicated below, a cyclic phosphinidene compound may be formed as a by-product and as will be appreciated, such a by-product will contain more than one P-P bond.

[0027] Thus in one embodiment, the present invention comprises subjecting a heterometallic phosphinidene complex to a thermal decomposition reaction, wherein the heterometallic phosphinidene comprises:

(i) a plurality of phosphinidene ligands, [PR] wherein each R which may be the same or different, is selected from substituted or unsubstituted C_1 - C_{15} alkyl, alkenyl, alkynyl, cycloalkyl, aryl, aralkyl, and alkaryl, wherein the substituents may be F or alkylsilyl groups,
(ii) at least one metal selected from a Group 13, 14 or 15 metal;
(iii) at least one Group I metal selected from Li, Na, K, Rb, Cs; and
(iv) a plurality of labile, Lewis-base stabilising ligands, each of which may be the same or different, (and preferably as described above)

and said thermal decomposition process results in the co-production of a cyclic phosphinidene compound $[PR]_n$, wherein n = 4-6.

[0028] A particularly preferred process according to the invention comprises subjecting a heterometallic phosphinidene complex to a thermal decomposition reaction, wherein the heterometallic phosphinidene complex comprises:

(i) a plurality of phosphinidene ligands, [PR] wherein each R which may be the same or different, is selected from substituted or unsubstituted C_1 - C_{15} alkyl, alkenyl, alkynyl, cycloalkyl, aryl, aralkyl, and alkaryl, wherein the substituents may be F or alkylsilyl groups,

(ii) at least one metal selected from Ge, Sn, Pb, As, Sb and Bi.

(iii) at least one metal selected from Li, Na, K, Rb and Cs,

(iv) a plurality of labile, Lewis-base stabilising ligands, each of which may be the same or different,

and said thermal decomposition process results in the co-production of a cyclic phosphinidene compound $[PR]_n$ wherein n = 4-6.

[0029] In the above embodiments R preferably contains 4 to 10 carbon atoms.

[0030] Preferably the phosphinidene compound has the formula $(M^1)_n(M^2)_m(Lg)_p(PR)_r$, wherein M^1 is a metal of Group 13, 14 or 15 of the Periodic Table, M^2 is a metal of Group 1 of the Periodic Table, PR is a phosphinidene ligand, Lg is a Lewis base ligand and each of n, m, p and r are in the range 1 to 10.

[0031] In the above formula, M^1 is preferably As, Sb and Bi and M^2 is preferably Li, Na, K or Rb. The group "R" in the phosphinidene ligand (PR) is preferably as defined above. Also, in the above formula, Lg is a Lewis base ligand which may be a primary, secondary or tertiary amine of formula $R^1R^2R^3N$, wherein each of R^1, R^2 and R^3 represent hydrogen, C_1-C_{10} alkyl or C_6-C_{10} aryl group. In addition other Lewis bases such as polyamines [e.g. ethylenediamine $(H_2NCH_2)_2$], permethylated polyamines (for example TMEDA $\{[(CH_3)_2NCH_2]_2\}$ and PMDETA $\{[(CH_3)_2NCH_2CH_2]_2NCH_3\}$, pyridines ($C_5H_5N$) or polypyridines (such as 2,2'-bipyridine, $(C_5H_4N)_2$ may be employed. Oxygen donors such as ethers (e.g. tetrahydrofuran, THF) may also be used.

[0032] In exemplary phosphinidene compounds, the ratios of m:n may vary from 4:1 to 1:4. Typically, m and n are 1, 2, 3 or 4, thus in phosphinidene compounds which are especially useful as starting materials, m may be 1 and n may be 3. In other phosphinidene compounds of interest, m is 1 and n is 2, or m and n are both 1. The integers p and r are typically in the range 4 to 8 and in exemplary compounds, both p and r are 6.

[0033] Especially preferred heterometallic phosphinidene compounds suitable for use in the process of the invention may be represented by the formula $[Sb(PCy)_3]_2Li_6.6Me_2NH.2C_6H_5CH_3$ (**I**), $\{[cyclo\text{-}(CyP)_4Sb]Na.Me_2NH.TMEDA\}_2$ (**IV**) and $\{[cyclo\text{-}(^tBuP)_3As]Li.TMEDA.THF\}$ (**VI**).

[0034] It is preferred that the thermal decomposition process is carried out at a temperature of greater than 20 °C, and preferably at a temperature range of between 25-100 °C. The decomposition is preferably carried out with the phosphinidene compound in solution in an organic solvent such as a hydrocarbon (e.g. an n-alkane, such as n-hexane), an aromatic hydrocarbon (e.g. toluene) or tetrahydrofuran (THF).

[0035] Where the heterometallic phosphinidene complexes of the invention either contain stabilising Lewis base ligands, or stabilising Lewis base ligands which are aprotic (e.g. TMEDA, PMDETA, pyridines, polypyridines and oxygen donors such as ethers), the decomposition process may require activation. The activation procedure typically comprises subjecting the heterometallic phosphinidene complex to thermal decomposition as described above, in the presence of a primary or secondary amine (e.g. Me_2NH) added separately to the complex.

[0036] In preferred embodiments of the invention, the thermal decomposition process results in the'formation of a Zintl compound comprising a polymetallic anion consisting of atoms of one or more metals. In many instances, the polymetallic anion is coordinated with metal cations, and the metal cations are coordinated with Lewis base ligands. The Zintl compounds formed typically comprise a polymetallic anion consisting of atoms of a metal M^1, wherein said polymetallic anion may or may not be coordinated with cations of a metal M^2, and the cations of a metal M^2 are coordinated with Lewis base ligands Lg. In other examples of Zintl compounds, the cation may be separated from the polymetallic anion. Thus as described in "Polyatomic Zintl Anions of the Post-Transition Elements", Corbett, J.D., *Chem. Rev.,* 1985, 85, 385-397, a wide variety of different structures is possible. Thus where the ligand:alkali metal cation ratio is high, or when polyether or cryptand ligands are present, the cations may be "separated" by their coordination to the Lewis base ligands, so the cation is separated from the polymetallic anion.

[0037] Preferably the Zintl compound has the formula $(M^1)_{n'}(M^2)_{m'}(Lg)_{p'}$, wherein M^1, M^2 and Lg are as defined above and each of n', m' and p' are in the range 1 to 10. M^1 is preferably a metal of Group 13, 14 or 15 of the Periodic Table. Especially preferred metals are those in Group 15, in particular As, Sb and Bi. M^2 may be a metal of Group 1 of the Periodic Table, preferably Li, Na, K or Rb. Lg is preferably a Lewis base ligand which may be a primary, secondary or tertiary amine of formula $R^1R^2R^3N$, wherein each of R^1, R^2 and R^3 represent hydrogen, C_1-C_{10} alkyl or C_6-C_{10} aryl group. In addition other Lewis bases such as polyamines [e.g. ethylenediamine $(H_2NCH_2)_2$], permethylated polyamines (for example TMEDA $\{[(CH_3)_2NCH_2]_2\}$ and PMDETA $\{[(CH_3)_2NCH_2CH_2]_2NCH_3\}$, pyridines ($C_5H_5N$) or polypyridines (such as 2,2'-bipyridine, $(C_5H_4N)_2$ may be employed. Oxygen donors such as ethers (e.g. tetrahydrofuran, THF) may also be used.

[0038] In exemplary Zintl compounds, the ratios of m':n' may vary from 5:1 to 1:5. Typically, m' and n' are 4-9, thus in the Zintl compound of formula (**II**) n' is 7 and m' is 3. The integer p' depends on the metal M^2 and the number of donor atoms in Lg and may be 1-8. The pre-

cise stoichiometry of the Zintl compound will depend on the nature and identity of the phosphinidene compound used as starting material (or where more than one phosphinidene compound is used, also on the ratio of different phosphinidene compounds used) and also on the identity of the Lewis acid base. Thus, by varying these parameters, a range of different Zintl compounds may be produced.

[0039] In accordance with a second aspect of the invention there is provided the use of a stable heterometallic phosphinidene complex as described above as a precursor for the deposition of a film containing an intermetallic compound.

[0040] In accordance with a third aspect the invention there is provided a process for the production of an intermetallic compound comprising:

(a) forming a Zintl compound by a method described above, the Zintl compound comprising a polymetallic anion consisting of atoms of a metal M^1, and cations of a metal M^2 which are coordinated with stabilising ligands Lg, and
(b) subsequently removing the stabilising ligands.

[0041] It is preferred that the stabilising ligand is a Lewis base, for example, one of the preferred Lewis bases referred to above. Advantageously, the stabilising ligands may be removed under reduced pressure or by evaporation at atmospheric pressure.

[0042] According to the invention, a preferred process for the production of an intermetallic alloy comprises:

(a) forming a Zintl compound by subjecting a heterometallic phosphinidene complex as described above to thermal decomposition, said Zintl compound comprising a polymetallic anion consisting of atoms of a metal M^1, and cations of a metal M^2 which are coordinated with stabilising ligands Lg, and
(b) subsequently removing the stabilising ligands.

[0043] A further embodiment of the invention provides a method for forming an intermetallic layer on a surface or surface portion of an electronic device, which method comprises:

(a) applying a Zintl compound to the surface, said Zintl compound comprising a polymetallic anion consisting of atoms of a metal M^1, and cations of a metal M^2 which are coordinated with stabilising ligands Lg, and
(b) subsequently removing the stabilising ligands.

[0044] Another embodiment of the invention provides a method for forming an intermetallic layer on a surface or surface portion of an electronic device, which method comprises:

(a) applying a heterometallic phosphinidene compound to the surface, said heterometallic phosphinidene compound being as defined above in connection with the general and preferred aspects of the invention,
(b) subjecting the heterometallic phosphinidene compound to thermal decomposition with concomitant loss of stabilising ligands.

[0045] It will be appreciated that in the above-mentioned thermal decomposition, there will normally initially be formed a Zintl compound, said Zintl compound comprising a polymetallic anion consisting of atoms of a metal M^1 and cation of a metal M^2 which are coordinated with stabilising ligands, and that the stabilising ligands will subsequently be lost.

[0046] The formation of the Zintl compound and the subsequent loss therefrom of the stabilising ligands may be a single or a two step process. Where the formation of the Zintl compound and removal of the stabilising ligand occurs in two steps, this embodiment of the invention may be defined in terms of a method for forming an intermetallic layer on a surface or surface portion of an electronic device, which method comprises:

(a) applying a heterometallic phosphinidene compound to the surface, said heterometallic phosphinidene compound being defined above in connection with the general and preferred aspects of the invention,
(b) subjecting the heterometallic phosphinidene compound to thermal decomposition to a Zintl compound, said Zintl compound comprising a polymetallic anion consisting of atoms of a metal M^1 and cation of a metal M^2 which are coordinated with stabilising ligands, and
(c) subsequently removing the stabilising ligands.

[0047] A still further embodiment of the invention provides a method of manufacturing an electronic device having an intermetallic layer on a surface portion thereof, which comprises:

(a) applying a Zintl compound to the surface, said Zintl compound comprising a polymetallic anion consisting of atoms of a metal M^1 and cation of a metal M^2 which are coordinated with stabilising ligands Lg, and
(b) subsequently removing the stabilising ligands.

[0048] In the above described methods for forming an intermetallic layer on a surface or a surface portion of an electronic device, the application of a Zintl compound or a heterometallic phosphinidene compound to such a surface, is preferably carried out by a technique such as spin coating, dip coating, vacuum evaporation or electrospray.

[0049] in these embodiments, the precise manner in

which the polymetallic anion and the metal M^2 are arranged will depend on the identities of M^1 and M^2 and the identities of the ligand(s). In many instances, the polymetatlic anion will be coordinated with cations of metal M^2.

[0050] As it will be appreciated, the ratio of metals in the heterometallic phosphinidene compound can be varied depending upon the ratio of starting materials and conditions in which they are synthesised. The thermal decomposition process of the invention will therefore produce a Zintl compound whose ratio of M^1 and M^2 (if not necessarily the same as that present in the phosphinidene compound) will be dictated by the individual chemical pathway of the decomposition.

[0051] Subsequent removal of the Lewis base stabilising ligands from the Zintl compound will produce an intermetallic compound having a metal composition which is therefore dictated by that of the heterometallic phosphinidene compound. Thus an important feature of the process of the invention is the possibility of selecting a heterometallic phosphinidene compound to produce an intermetallic compound having the desired metal stoichiometry. As discussed above, the photoactive properties of intermetallic compounds are determined by the stoichiometries of the metal components.

[0052] The nature and composition of the intermetallic layer may be adapted to confer desired electrical properties depending upon the electronic device for which it is to be applied to. By using different phosphinidene precursors or Zintl compounds or mixtures thereof, intermetallic layers with different proportions of metals may be formed. Intermetallic layers, in particular, those comprising an alkali metal and one or more metals selected from those of Group 13, Group 14 or Group 15 of the Periodic Table (especially in stoichiometric quantities) are particularly useful in such applications, as they possess highly desirable photoactive characteristics. Particularly useful is the application of intermetallic layers having electron emitter properties, such as those required by photoelectric devices. For example, intermetallic alkali metal antimonide films have wide applications as batteries and photoactive materials in photomultipliers which are used e.g. (1) medical scanners, (2) scientific instruments, and (3) particle physics.

[0053] Structural formulae of exemplary compounds are given in the accompanying drawings (Figures 1-6).

Figure 1 Structure of heterometallic phosphinidene compound $[Sb(PCy)_3]_2Li_6.6HNMe$ (**I**).

Figure 2 Structure of Zintl compound $[Sb_7Li_3.6HNMe_2]$ (**II**).

Figure 3 Structure of Zintl compound $\{[(TMEDA)Li]_3Sb_7\}$ (**III**).

Figure 4 Structure of $\{[CyP]_4SbNa.TMEDA.Me_2NH\}_2$ (**IV**).

Figure 5 Structure of $[Sb_7Na_3.3TMEDA.3THF]$ (**V**).

Figure 6 Structure of heterometallic phosphinidene compound $\{cyclo\text{-}[(^tBuP)_3As]Li.TMEDA.THF\}$ (**VI**).

Figure 7 Schematic representation of the LiSb photodiode test cell.

Figure 8 Plot of the quantum efficiency values which are corrected for vacuum envelope transmission function, as a function of the wavelength.

The production of Zintl compounds in accordance with the invention and their conversion to intermetallic compounds is described in the following Examples.

EXAMPLES

1. Synthesis of $[Sb(PCy)_3]_2Li_6.6HNMe_2.2C_6H_5CH_3$ (I)

[0054] To a stirred and chilled suspension of $[LiPHCy]_n$ (7.53 mmol of monomer) in toluene (5 ml) was added to a solution of $[Sb(NMe_2)_3]$ (2.51 mmol, 1.36 cm^3, 1.84 mol dm^{-3} in toluene),

[0055] The suspension was stirred and gradually allowed to warm towards 0 °C at which stage a yellow precipitate was observed. This was dissolved by the addition of chilled toluene (8 cm^3) and THF (1 cm^3). The red solution produced was stored at -35 °C for 48 hr over which period crystals suitable for X-ray diffraction studies grew.

[0056] The following data refer to this material: yield 1.02 g (57%); decomp. 170 °C; IR(Nujol), major bands at 1257(m), 1178(s), 1051(s), 992.5(m), 897(s), 846(s), 730(m), 694(w); ^1H NMR (400.16 MHz, +25 °C, $C_6D_5CD_3$), δ = 7.0 (5H, mult., aryl C-H, $C_6H_5CH_3$), 3.94 (13H, s., Me, Me_2NH), 2.5-1.2 (33H, overlapping mult., Cy and $C_6H_5CH_3$ Me group (2.10)); ^7Li NMR (155.513 MHz, +25 °C, $C_6D_5CD_3$), δ = 5.57 (binomial sept., $^1J^{31}_{p\text{-}^7Li}$ = 14 Hz) (rel. to $LiCl/D_2O$) (7.14 rel. to $PhLi/C_6D_5CD_3$); ^{31}P NMR (162.000 MHz, +25 °C, $C_6D_5CD_3$), δ = -263.5 (rel. to neat $(MeO)_3P$; br. s., width at half height 1130 Hz); Elemental analysis calc. C 52.3, H 8.7, N 5.6, found C 52.0, H 8.4, N 4.4.

[0057] Crystal data for **I**; $C_{31}H_{62}Li_3N_3P_3Sb$, M = 712.32, space group monoclinic $P2_1/c$, α = 13.460(3), β = 18.123(3), γ = 16.589(4)Å, b = 99.83(2)°, V= 3987(2) Å^3, Z = 4, ρ_{calc} = 1.187 Mgm^{-3}, T = 150(2)K, μ(Mo-Kα) = 0.834 mm^{-1}, F(000) = 1496. Yellow cubes, crystal dimensions 0.30x0.25x0.20 mm. 3717 reflections ($2q$ < 45.0°) were collected on a Siemens R3mV diffractometer using Mo-Kα radiation (λ = 0.71073 Å), graphite monochromator and $\theta/2\omega$ scans ($2.57 \leq \theta \leq 19.99°$). 3717 independent reflections (R_{int}= 0.021) after a semi-empirical absorption correction was applied. The structure was solved using direct methods and refined by full matrix least squares based on F^2(SHELXL93), with all non-hydrogen atoms assigned anisotropic displacement parameters; cyclohexyl, toluene and amine H atoms were fixed in idealised positions and allowed to ride on the relevant C or N atoms. The refinement converged to $R1$ = 0.0748 for data F > 4σ/(F) and $wR2$ = 0.2722

for all data, goodness of fit = 1.013, and weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0597P)^2 + 18.32P]$, where $P = (F_o^2 + 2F_c^2)/3$. Largest peak and hole in the final difference map; 0.913, -0.689 eÅ^{-3}. Crystals of **I** were weakly diffracting. Restraints were applied for the lattice-bound toluene which is disordered over two (50:50) sites about a two-fold axis.

[0058] If **I** is subjected to a vacuum (*ca*. 10^{-3} atm, 15 min), almost all the Me_2NH is removed, giving the unsolvated complex {[Sb(PCy)$_3$]Li$_6$} [**I***].

2. Thermal Decomposition of [Sb(PCy)$_3$]$_2$Li$_6$.6HNMe$_2$.2C$_6$H$_5$CH$_3$ (I) to [Sb$_7$Li$_3$.6HNMe$_2$] (II)

[0059] A solution of [Sb(PCy)$_3$]$_2$Li$_6$.6HNMe$_2$ (**I**) (1.0g, 1 mmol) in toluene (10 ml) was stirred at 30-40 °C for 10 min, giving a deep red solution and with almost all of the starting material dissolving. Cold filtration (*ca.* 0 °C) followed by storage of the filtrate at -35 °C (48 hr) gave a large crop of deep red plates of [Sb$_7$Li$_3$.6HNMe$_2$] (**II**). Although **II** is too thermally unstable at 25 °C to be isolated as a pure material, the yield is almost quantitative.

[0060] X-ray data for **II**; $C_{12}H_{42}Li_3N_6Sb_7$, *M*= 1143.58, trigonal, space group *P*-3, α = 11.508(1), γ = 14.954(2) Å, *Z* = 1, $\rho_{calc.}$ = 2.214 Mgm^{-3}, λ = 0.71073 Å, *T* = 198 (2)K, μ(Mo-Kα) = 5.438 mm^{-1}, *F*(000) = 1044. Data were collected on a Siemens P4 diffractometer using an oil-coated rapidly-cooled crystal of dimensions 0.10x0.36x0.48 mm by the $\theta/2\omega$ method ($1.36° \le \theta \le 25.00°$). Of a total of 4482 collected reflections, 2004 were independent (R_{int} = 0.048). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1(F>4\sigma/(F))$ = 0.053 and *wR*2 = 0.168 (all data); largest peak and hole in final difference map 2.038 and -1.402eÅ^{-3}.

2A. Thermal decomposition of [Sb(PCy)$_3$]Li$_6$} [I*]to [Sb$_7$Li$_3$.6HNMe$_2$] (II)

[0061] Neat liquid Me_2NH was added to a dilute THF solution of [Sb(PCy)$_3$]Li$_6$} [**I***] at a temperature of 25 °C or below. Decomposition of [**I***] to Zintl compound (**II**) occurs immediately.

3. Synthesis of {[(TMEDA)Li]$_3$Sb$_7$} (III)

[0062] Excess TMEDA (*ca.* 1 ml) was added to a deep red solution of [Sb$_7$Li$_3$.6HNMe$_2$] (**II**), prepared as described in Example 2 or Example 2A. Storage at -35 °C (12 hr) produced a large crop of red crystalline plates of {[(TMEDA)Li]$_3$Sb$_7$} (**III**). The yield of **III** is quantitative.

[0063] X-ray data for **III;** $C_{32}H_{64}Li_3N_6Sb_7$, *M*= 1407.97, monoclinic, space group *P*21/*m*, α = 10.192 (1), β = 20.944(3), γ = 11.967(2) Å, *b* = 92.22(1)°, *Z* = 4, $\rho_{calc.}$ = 1.829 Mgm^{-3}, λ = 0.71073 Å, *T* = 213(2) K, μ(Mo-Kα) = 3.673 mm^{-1}, *F*(000) = 1328. Data were collected on a Siemens P4 diffractometer using an oil-coated rapidly-cooled crystal of dimensions 0.20x0.35x0.40 mm by the $\theta/2\omega$ method ($1.94° \le \theta \le 25.00°$). Of a total of 4636 collected reflections, 5803 were independent (R_{int} = 0.051). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1$ ($F>4\sigma/(F)$) = 0.066 and *wR*2 = 0.241 (all data) [$R1 = \Sigma^{!}F_o - F_c^{!}/\Sigma F_o$ and $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma\omega(F_o^2)^2)^{0.5}$, $w = 1/[\sigma^2(F_o^2) + (yP)^2 + xP]$, $P = F_o^2 + (2F_c^2/3)$]; largest peak and hole in final difference map 1.772 and -2.419eÅ^{-3}. The -CH_2- and Me groups of all the TMEDA ligands are disordered over two 1:1 sites. The disordered toluene molecule is disordered over two sites about a two-fold axis.

[0064] The formation of [CyP_4] along with **II** and **III** was confirmed by determination of the unit cell. The parameters are in agreement with those obtained in the literature (Bart, J.C.J., *Acta. Crystallogr.* Section B, 1969, 25, 762).

4. Formation of Intermetallic Phase from [Sb$_7$Li$_3$.6HNMe$_2$] (II) or {[(TMEDA)Li]$_3$Sb$_7$}(III)

[0065] Storage of the Zinti compounds [Sb$_7$Li$_3$.6HNMe$_2$] **(II)** or {[TMEDA}Li]$_3$Sb$_7$}(**III**) at room temperature over a period of time leads to a slow loss of amine ligand to form a lustrous intermetallic phase, comprising LiSb and Sb. When either complex is stored under vacuum, the loss of amine ligand occurs more rapidly (*ca*. 15 min, at 10^{-3} atm.).

5. Synthesis of {[cyclo-(CyP)$_4$Sb]Na.Me$_2$NH.TMEDA}$_2$ (IV)

[0066] [Sb(NMe$_2$)$_3$] (5.1 ml, 1.74 mol dm^{-3} in toluene, 8.8 mmol) was added dropwise to a chilled solution of $CyPH_2$ (1.17 ml, 8.8 mmol) in hexane (20 ml). The solution was allowed to warm to room temperature and stirred (10 mins). The orange solution produced was transferred by syringe into a chilled (*ca*. -20 °C) solution of [CyPHNa] (prepared *in situ* by the reaction of $PhCH_2Na$ (1.0 g, 8.8 mmol) with $CyPH_2$ (1.17 ml, 8.8 mmol) in hexane (10 ml)/THF (5 ml)). The reaction mixture was allowed to warm to ca. 0 °C. Excess TMEDA (ca. 3.0 ml, 20 mmol) was added and the solution was filtered while cold. Crystallisation at -35 °C (24 hrs) gave red plates of **IV.** Yield 1.1 g (16% on the basis of Sb supplied). Further crystallisation from the filtrate gave a mixture of **IV** and **V** (as black cubic crystals). Decomp. 75 °C. ^{1}H NMR (+25 °C, 250 MHz, D_8 toluene), 1.0-2.0 (overlapping mult., 40H, {CyP}$_4$), 2.22 (d., 4H ($^2J^{31}_{P\text{-}H}$ *ca*. 6.4Hz), C(α)-H of {CyP}$_4$), 2.10 (br. s., 16H, TMEDA), 2.46 (s., 6H, Me_2NH). Elemental analysis; calcd. C 50.4, H 8.8, N 5.5, P 16.3, found C 49.0, H 8.6, N 5.2, P 15.1.

[0067] Crystal data for **IV:** $C_{32}H_{67}N_3P_4Sb$, *M*= 762.51, monoclinic, space group $P2_1/n$, α = 11.168(3), β = 22.420(4), γ = 16.468(3)Å, β- = 92.71(2)°,*U* = 4119(1) Å^3, *Z* = 4, $\rho_{calc.}$ = 1.230 Mgm^{-3}, λ = 0.71073 Å, *T* = 223 (2)K, μ(Mo-Kα) = 0.859 mm^{-1}, *F*(000) = 1608. Data were

collected on a Siemens P4 diffractometer using an oil-coated rapidly-cooled crystal of dimensions 0.35x0.30x0.20 mm by the $\theta/2\omega$ method ($1.82° \leq \theta \leq 25.01°$). Of a total of 7257 collected reflections, 7257 were independent (R_{int}= 0.073). Empirical absorption corrections were applied after initial refinement with isotropic displacement parameters (max., min. transmission 0.982, 0.778). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1$ ($F>4\sigma(F)$) = 0.079 and $wR2$ = 0.271 (all data) [$R1 = \Sigma^{l}F_o - F_c^{l}/\Sigma F_o$ and $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)^{0.5}$, $w = 1/[\sigma^2(F_o^2) + (yP)^2 + xP]$, $P = F_o^2 + (2F_c^2/3)$] largest peak and hole in the final difference map 0.808 and -0.844eÅ^{-3}.

6. Formation of [Sb_7Na_3.3TMEDA.3THF] (V)

[0068] Example 5 was repeated using the same method and volumes of solvent, but the quantities of reagents were doubled and the solution was briefly brought to reflux prior to storage at -35 °C (24 hrs) to obtain complex (**V**). Yield 3.5 g (96% on the basis of the Sb supplied). The complex is stable at 25 °C.

[0069] Crystal data for **V**; $C_{30}H_{72}N_6Na_3O_3Sb_7$, M = 1486.16, monoclinic, space group $P2(1)/m$, Z=2, a = 10.207(3), b = 22.101(6), c = 11.719(3)Å, β = 92.249(19)°, U = 2641.7(11)Å^3, ρ_{calc} = 1.868 Mgm^{-3}, μ(Mo-Kα) =3.581 mm^{-1}, T = 223(2) K, F(000) = 1416. Data were collected on a Siemens P4 diffractometer on an oil-coated crystal of dimensions 0.40 x 0.40 x 0.30 mm ($1.97 \leq \theta \leq 21.00$). Of a total of 3779 data collected, 2935 were independent (R_{int} = 0.098). An empirical absorption correction was applied. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of R1 [$I>2\sigma(I)$] = 0.086, ωR2 = 0.230 (all data). Largest difference between peak and hole 1.444, -1.076 eÅ^{-3}.

7. Preparation of {*cyclo*-[(^{t}BuP)$_3$As]Li.TMEDA.THF} (VI)

[0070] [(^{t}BuPH$_2$ was prepared by an original method using the reaction of ^{t}BuPCl$_2$ with $LiAlH_4$ (1:2 eqiv.) in 1,4-dioxane. Double-distillation (760 mmHg) gave *ca.* 30-40% yields of the phosphine (boiling range 65-70 °C).

***Synthesis of (VI)*:**

[0071] To a stirred, chilled suspension of [LiPH^{t}Bu]$_n$ (6.0 mmol of monomer) in toluene (20 ml) and TMEDA (1.0 ml) was added a solution of [As(NMe$_2$)$_3$] (2.0 mmol, 0.92 cm^3, 2.17 mol dm^{-3} in toluene). The suspension was stirred and gradually allowed to warm to 0 °C, at which stage an orange precipitate was observed. THF (20ml) was added and the mixture stirred for 48 h after which an orange solution (with a fine precipitate) remained. This was filtered and the solvent removed to ca. 8 ml. The solid produced was redissolved by the addition of THF (*ca*. 1 ml) and storage at -18 °C (12 h) gave orange crystals of (**VI**) suitable for X-ray diffraction studies; yield 0.27 g (25% on the basis of As supplied to the reaction); mp. 115 °C to clean to clean orange oil; IR (Nujol), major bands at 1260(m), 1032(s) cm^{-1}; ^{7}Li NMR (155.505 MHz, + 25 °C, D_8-THF, rel. PhLi/THF), δ = -2.71 (s.), ^{31}P NMR (161.969 MHz, +25°C, D_8-THF; rel. to 80% H_3PO_4/D_2O), δ = 7.87 (t.), -74.50 (d.) (ratio 1: 2, $^1J_{^{31}P\text{-}^{31}P}$ = 179.4 ± 0.8 Hz); Elemental analysis calc. P 17.4, found P 17.6.

[0072] Crystal data for **VI**; $C_{22}H_{51}AsLiN_2OP_3$, M = 534.42, monoclinic, space group $P2_1/n$, a = 12.238(7), b = 15.574(12), c = 16.27(1), β = 105.23(5)°, V = 2993 (4) Å^3, Z = 4, D_{calc} = 1.186 Mgm^{-3}, T = 180(2)K, μ(Mo-Kα) = 1.311mm^{-1}, F(000) = 1144. Data on a crystal of dimensions 0.40 x 0.28 x 0.28 mm were collected on a Siemens-Stoe diffractometer using ω/θ scans ($3.56 \leq \theta \geq 22.50$). Of a total of 7645 reflections, 3900 were independent (R_{int} = 0.1036). The structure was solved using direct methods and refined by full matrix least squares on F^2 (SHELXL 93) to final R indices of $R1$ = 0.086 [$F > 4\sigma(F)$] and $wR2$ = 0.200 [all data]. The C atoms of the THF ligand and one of the C atoms of each of the MeN groups of the TMEDA were disordered over two sites and were refined with half occupancy. H-atoms were fixed geometrically,

8. Manufacture of Photoelectric Device

Construction of demonstration cell:

[0073] A photoelectric device in the form of a LiSb photodiode test cell, as depicted in Figure 7, was constructed from a hollow glass cylinder 10, which has a constriction to allow the application of a vacuum at one end (shown sealed after evacuation in Figure 7) 12, and a flat glass deposition surface 14 at the other end. The inside surface of the glass cylinder was aluminised to form a thin film 16 in contact with the deposition surface 14. A LiSb intermetallic layer 18 was formed on the deposition surface 14 in accordance with any of the Methods A-C described below. The test cell was further equipped with a cathode contact 20 to the aluminised film 16 and a central anode ring 22.

Formation of intermetallic layer on test cell:

[0074] The intermetallic layer was formed on the test cell in accordance with one of the following methods A-C:

Method A:

[0075] A solution of II in THF (*ca.* 0.01 mol dm^{-3}) was carefully introduced onto the deposition surface through the constriction 12 (shown sealed in Figure 7) using a syringe so as to produce a solution surface of about 2

mm thick. The solvent was evaporated under vacuum from the deposition surface under argon to produce a golden-brown metallic film 18 on the deposition surface 14.

Method B:

[0076] A solution of **I** in THF (*ca.* 0.01 mol dm^{-3}) was carefully introduced onto the deposition surface through the constriction 12 (shown sealed in Figure 7) using a syringe so as to produce a solution surface of about 2 mm thick. The solution was allowed to stand at a temperature of 30-40 °C in an argon atmosphere on a vacuum line to produce the same lustrous intermetallic film 18 as formed in Method A.

Method C:

[0077] A solution of **II** suitable for use in accordance with the procedure described in Method A was formed from a THF solution of the unsolvated complex [Sb$(PCy)_3]Li_6$} [**I***] by the method described in Example 2A.

Measurement of photosensitivity and spectral response of the Li/Sb test cell:

[0078] After construction of the test cell and formation of the intermetallic layer as described above, the test cell was evacuated to 10^{-6} torr and the constriction 12 was flame sealed.

[0079] The photoelectric spectral response of the intermetallic layer was measured between 270 and 450 nm. Table 1 shows the quantum efficiency (expressed as a percentage) of the LiSb intermetallic compound after correction for the variation in optical transmission of the glass cylinder.

TABLE 1.

Photosensitivity results for Sb/Li	
Wavelength (nm)	Quantum Efficiency
270	1.35887
280	0.67085
290	0.46643
300	0.35504
310	0.30607
320	0.24717
330	0.26335
340	0.25002
350	0.19304
360	0.18368
370	0.03239

TABLE 1. (continued)

Photosensitivity results for Sb/Li	
Wavelength (nm)	Quantum Efficiency
380	0.01079
390	0
400	0
410	0
420	0
430	0
440	0
450	0

[0080] The data from Table 1 are represented graphically in Figure 8. Figure 8 shows the corrected quantum efficiency of the LiSb test cell against wavelength after the transmission function of the vacuum envelope has been taken into account. The graph shows the onset of spectral response to be around 3.2 eV (for 390 nm), demonstrating the formation of a photosensitive LiSb intermetallic layer.

Claims

1. A process for the production of a Zintl compound comprising subjecting a heterometallic phosphinidene complex to thermal decomposition.

2. A process according to Claim 1 wherein the heterometallic phosphinidene complex comprises at least two metals.

3. A process according to Claim 2 wherein one of said metals is a metal of Group 13, 14 or 15 of the Periodic Table.

4. A process according to Claim 3 wherein one of said metals is a metal of Group 15 of the Periodic Table.

5. A process according to Claim 3 wherein one of said metals is selected from As, Sb and Bi.

6. A process according to Claim 2 wherein one of said metals is a metal of Group 1 of the Periodic Table.

7. A process according to Claim 6 wherein one of said metals is Li, Na, K, Rb or Cs.

8. A process according to any preceding claim wherein the heterometallic phosphinidene complex contains one or more phosphinidene ligands, which may be the same or different, and having a phosphorus atom covalently linked to a substituted or un-

substituted hydrocarbyl group.

9. A process according to Claim 8 wherein the substituted or unsubstituted hydrocarbyl group contains 1 to 15, preferably 4 to 10 carbon atoms.

10. A process according to Claim 9 wherein the substituted or unsubstituted hydrocarbyl group is selected from alkyl, alkenyl, alkynyl, cycloalkyl, aryl, aralkyl, alkaryl groups, wherein the substituent or substituents may be selected from fluoro or C_1-C_6 alkylsilyl groups.

11. A process according to any of Claims 8-10 wherein the heterometallic phosphinidene complex contains one or more phosphinidene ligands, having a phosphorus atom covalently linked to a cyclohexyl group.

12. A process according to any preceding claim wherein the phosphorus atom of the or each phosphinidene ligand is coordinated to four metal atoms.

13. A process according to Claim 12, wherein the phosphorus atom of the or each phosphinidene ligand is coordinated to three Group I metal atoms.

14. A process according to Claim 12 or Claim 13, wherein the phosphorus atom of the or each phosphinidene ligand is coordinated to one metal atom of Groups 13, 14 or 15.

15. A process according to any preceding claim wherein the heterometallic phosphinidene complex comprises a second ligand being a Lewis base.

16. A process according to Claim 15, wherein the Lewis base comprises one or more prirriary, secondary or tertiary amine groups or an ether group.

17. A process according to Claim 16, wherein the Lewis base is a primary, secondary or tertiary amine of the formula $R^1R^2R^3N$, wherein each of R^1, R^2 and R^3 represents hydrogen, a C_1-C_6 alkyl group or C_6-C_{10} aryl group, a polyamine, permethylated polyamine, pyridine or polypyridine, or tetrahydrofuran.

18. A process according to Claim 17, wherein the Lewis base is selected from dimethylamine, TMEDA {$[(CH_3)_2NCH_2]_2$} and PMDETA {$[(CH_3)_2NCH_2CH_2]_2NCH_3$}.

19. A process according to any preceding claim wherein the thermal decomposition results in the co-production of a phosphorus compound having at least one P-P bond.

20. A process according to Claim 16, wherein the co-produced phosphorus compound is a cyclic phosphinidene.

21. A process according to any preceding claim wherein the stable heterometallic phosphinidene complex comprises:

(i) a plurality of phosphinidene ligands, [PR], wherein each R which may be the same or different, is selected from C_1-C_6 alkyl, branched alkyl, cycloalkyl or aryl groups,
(ii) at least one metal selected from a Group 14 or Group 15 metal;
(iii) at least one Group I metal selected from Li, Na, K, Rb, Cs; and
(iv) a plurality of labile, Lewis-base stabilising ligands, each of which may be the same or different,

and said thermal decomposition process results in the co-production of a cyclic phosphinidene compound $[PR]_n$, where n = 4-6.

22. A process according to any preceding claim wherein the stable heterometallic phosphinidene complex comprises:

(i) a plurality of phosphinidene ligands, [PR], wherein each R which may be the same or different, is selected from C_1-C_6 alkyl, branched alkyl, cycloalkyl or aryl,
(ii) at least one metal selected from Ge, Sn, Pb, As, Sb and Bi.
(iii) at least one metal selected from Li, Na, K, Rb and Cs,
(iv) a plurality of labile, Lewis-base stabilising ligands, each of which may be the same or different,

and said thermal decomposition process results in the co-production of a cyclic phosphinidene compound $[PR]_n$, wherein n = 4-6.

23. A process according to any preceding claim wherein the thermal decomposition is carried out at a temperature of greater than 20 °C.

24. A process according to Claim 21 wherein the thermal decomposition is carried out at a temperature range of between 25-100 °C.

25. A process according to any preceding claim wherein the thermal decomposition is carried out with the phosphinidene compound in solution in an organic solvent.

26. A process according to any preceding claim wherein the organic solvent is selected from a hydrocar-

bon such as an n-alkane, an aromatic hydrocarbon such as toluene, or THF.

27. A process according to any preceding claim wherein the stable heterometallic phosphinidene complex may be represented by the formula $[Sb(PCy)_3]_2Li_6.6Me_2NH$, $\{[cyclo\text{-}(CyP)_4Sb]Na.Me_2NH.TMEDA]_2$, or $[(^tBuP)_3As.Li.TMEDA.THF]$, wherein Cy = cyclohexyl.

28. A process according to any preceding claim wherein the Zintl compound comprises a polymetallic anion consisting of atoms of one or more metals, wherein said polymetallic anion may optionally be coordinated with metal cations, and the metal cations are coordinated with Lewis base ligands.

29. A process according to Claim 28 wherein the Zintl compound comprises a polymetallic anion consisting of atoms of a metal M^1, wherein said polymetallic anion may optionally be coordinated with cations of a metal M^2, and the cations of a metal M^2 are coordinated with Lewis base ligands Lg.

30. A process according to Claim 28 wherein the Zintl compound has the formula $(M^1)_{n'}(M^2)_{m'}(Lg)_{p'}$, wherein M^1, M^2 and Lg are as defined in Claim 29 and each of n', m' and p' are in the range 1 to 10.

31. A process according to Claim 29 or Claim 30 wherein M^1 is a metal of Group 13, 14 or 15 of the Periodic Table.

32. A process according to Claim 29 wherein M^1 is a metal of Group 15 of the Periodic Table.

33. A process according to Claim 32 wherein M^1 is selected from As, Sb and Bi.

34. A process according to any of Claims 29 to 33 wherein M^2 is a metal of Group 1 of the Periodic Table.

35. A process according to Claim 34 wherein M^2 is Li, Na, K or Rb.

36. A process according to any of Claims 30 to 35, wherein the Lewis base Lg comprises one or more primary, secondary or tertiary amine groups or an ether group.

37. A process according to Claim 36, wherein the Lewis base Lg is a primary, secondary or tertiary amine of the formula $R^1R^2R^3N$, wherein each of R^1, R^2 and R^3 represents hydrogen, a C_1-C_6 alkyl group or C_6-C_{10} aryl group, a polyamine, permethylated polyamine, pyridine, polypyridine or tetrahydrofuran.

38. A process according to Claim 37, wherein the Lewis base Lg is selected from dimethylamine, TMEDA $\{[(CH_3)_2NCH_2]_2\}$ and PMDETA $\{[(CH_3)_2NCH_2CH_2)_2NCH_3\}$.

39. A process according to any preceding claim in which the phosphinidene complex is contacted with a primary or secondary amine prior to being subjected to thermal decomposition.

40. A process according to Claim 39 wherein the phosphinidene complex which is contacted with the primary or secondary amine is free of stabilising Lewis base ligands.

41. A process according to Claim 39 wherein the phosphinidene complex which is contacted with primary or secondary amine, contains a stabilising Lewis base ligand which is aprotic.

42. A process according to any of Claims 39-41 wherein the phosphinidene complex is contacted with dimethylamine.

43. A process for the production of an intermetallic compound comprising:

(a) forming a Zintl compound by a process according to any preceding claim, said Zintl compound comprising a polyatomic anion consisting of atoms of a metal M^1, wherein said polyatomic anion may optionally be coordinated with cations of a metal M^2, and the cations of a metal M^2 are coordinated with stabilising ligands Lg, and
(b) subsequently removing the stabilising ligands.

44. A process for the production of an intermetallic compound according to Claim 43, wherein the stabilising ligands are Lewis base ligands.

45. A process for the production of an intermetallic compound according to Claim 43 or Claim 44 wherein the stabilising ligands are removed under reduced pressure.

46. A process for the production of an intermetallic compound which comprises:

(a) forming a Zintl compound by subjecting a heterometallic phosphinidene complex to thermal decomposition, said Zintl compound comprising a polyatomic anion consisting of atoms of a metal M^1, wherein said polyatomic anion may optionally be coordinated with cations of a metal M^2, and the cations of a metal M^2 are coordinated with stabilising ligands Lg, and

(b) subsequently removing the stabilising ligands.

47. A process for the production of an intermetallic compound according to Claim 46 wherein the heterometallic phosphinidene complex is as defined in any of Claims 2-11.

48. A process for the production of an intermetallic compound according to Claim 46 or 47 wherein the Zintl compound is as defined in any of Claims 28 to 38.

49. A process for the production of an intermetallic compound according to any of Claims 46 to 48 wherein the thermal decomposition is carried out at a temperature of greater than 20 °C.

50. A process for the production of an intermetallic compound according to Claim 49 wherein the thermal decomposition is carried out at a temperature range of between 25-100 °C.

51. A process according to Claims 48-50 wherein the thermal decomposition is carried out with the phosphinidene compound in solution in an organic solvent.

52. A process according to Claim 51 wherein the organic solvent is selected from a hydrocarbon such as an n-alkane, an aromatic hydrocarbon such as toluene, or THF.

53. A method for forming an intermetallic layer on a surface which method comprises:

(a) applying a Zintl compound to the surface, said Zintl compound comprising a polyatomic anion consisting of atoms of a metal M^1, wherein said polyatomic anion is coordinated with cations of a metal M^2, and the cations of a metal M^2 are coordinated with stabilising ligands Lg, and
(b) subsequently removing the stabilising ligands.

54. A method for forming an intermetallic layer on a surface which method comprises:

(a) applying a heterometallic phosphinidene compound to the surface, said heterometallic phosphinidene compound being as defined in any of Claims 1 to 22,
(b) subjecting the heterometallic phosphinidene compound to thermal decomposition with concomitant loss of stabilising ligand.

55. A method for forming an intermetallic layer on a surface which method comprises:

(a) applying a heterometallic phosphinidene compound to the surface, said heterometallic phosphinidene compound being as defined in any of Claim 1 to 22,
(b) subjecting the heterometallic phosphinidene compound to thermal decomposition to a Zintl compound, said Zintl compound comprising a polyatomic anion consisting of atoms of a metal M^1 and cation of a metal M^2 which are coordinated with stabilising ligands, and
(c) subsequently removing the stabilising ligands.

56. A method according to any of Claims 53-55, wherein said surface is a surface portion of an electronic device.

57. A method for manufacturing an electronic device having an intermetallic layer on a surface portion thereof, which comprises:

(a) applying a Zintl compound to the surface, said Zintl compound comprising a polyatomic anion consisting of atoms of a metal M^1, wherein said polyatomic anion may optionally be coordinated with cations of a metal M^2, and the cations of a metal M^2 are coordinated with stabilising ligands Lg, and
(b) subsequently removing the stabilising ligands.

58. A method for forming an intermetallic layer on a surface or surface portion of an electronic device, which method comprises:

(a) applying a heterometallic phosphinidene compound to the surface, said heterometallic phosphinidene compound being as defined in any of Claims 1 to 22,
(b) subjecting the heterometallic phosphinidene compound to thermal decomposition with concomitant loss of stabilising ligand.

59. A method for manufacturing an electronic device having an intermetallic layer on a surface portion thereof, which comprises:

(a) applying a heterometallic phosphinidene compound to the surface, said heterometallic phosphinidene compound being as defined in any of Claims 1 to 22,
(b) subjecting the heterometallic phosphinidene compound to thermal decomposition to a Zintl compound, said Zintl compound comprising a polyatomic anion consisting of atoms of a metal M^1 and cation of a metal M^2 which are coordinated with stabilising ligands, and
(c) subsequently removing the stabilising lig-

ands.

60. A method according to any of Claims 57-59, wherein the intermetallic layer in use is adapted to act as an electron emitter.

61. A method according to any of Claims 57-59, wherein the electronic device is a photoelectric device.

62. Use of a stable heterometallic phosphinidene complex as a precursor for the deposition of an intermetallic alloy film.

63. Use of a stable heterometallic phosphinidene complex as defined in any of Claims 2 to 36 as a precursor for the deposition of an intermetallic alloy film.

Patentansprüche

1. Verfahren zur Herstellung einer Zintl-Verbindung, bei dem ein heterometallischer Phosphinidenkomplex einer thermischen Zersetzung unterzogen wird.

2. Verfahren nach Anspruch 1, bei dem der heterometallische Phosphinidenkomplex mindestens zwei Metalle umfasst.

3. Verfahren nach Anspruch 2, bei dem eines der Metalle ein Metall der Gruppe 13, 14 oder 15 des Periodensystems ist.

4. Verfahren nach Anspruch 3, bei dem eines der Metalle ein Metall der Gruppe 15 des Periodensystems ist.

5. Verfahren nach Anspruch 3, bei dem eines der Metalle aus As, Sb und Bi ausgewählt ist.

6. Verfahren nach Anspruch 2, bei dem eines der Metalle ein Metall der Gruppe 1 des Periodensystems ist.

7. Verfahren nach Anspruch 6, bei dem eines der Metalle Li, Na, K, Rb oder Cs ist.

8. Verfahren nach einem der vorstehenden Ansprüche, bei dem der heterometallische Phosphinidenkomplex einen oder mehrere Phosphinidenliganden aufweist, die gleich oder voneinander verschieden sein können und ein Phosphoratom aufweisen, das kovalent mit einer substituierten oder unsubstituierten Hydrocarbylgruppe verbunden ist.

9. Verfahren nach Anspruch 8, bei dem die substituierte oder unsubstituierte Hydrocarbylgruppe 1 bis 15 vorzugsweise 4 bis 10 Kohlenstoffatome aufweist.

10. Verfahren nach Anspruch 9, bei dem die substituierte oder unsubstituierte Hydrocarbylgruppe aus Alkyl-, Alkenyl-, Alkynyl-, Cycloalkyl-, Aryl-, Aralkyl- und Alkarylgruppen ausgewählt ist, wobei der Substituent oder die Substituenten aus Fluor- oder C_1-C_6-Alkylsilylgruppen ausgewählt sein können.

11. Verfahren nach einem der Ansprüche 8 bis 10, bei dem der heterometallische Phosphinidenkomplex einen oder mehrere Phosphinidenliganden enthält, in denen ein Phosphoratom kovalent an eine Cyclohexylgruppe gebunden ist.

12. Verfahren nach einem der vorstehenden Ansprüche, bei dem das Phosphoratom des oder jedes Phosphinidenliganden an vier Metallatome koordiniert ist.

13. Verfahren nach Anspruch 12, bei dem das Phosphoratom des oder jedes Phosphinidenliganden an drei Metallatome der Gruppe I koordiniert ist.

14. Verfahren nach Anspruch 12 oder 13, bei dem das Phosphoratom des oder jedes Phosphinidenliganden an ein Metallatom der Gruppen 13, 14 oder 15 koordiniert ist.

15. Verfahren nach einem der vorstehenden Ansprüche, bei dem der heterometallische Phosphinidenkomplex einen zweiten Liganden umfasst, bei dem es sich um eine Lewis-Base handelt.

16. Verfahren nach Anspruch 15, bei dem die Lewis-Base eine oder mehrere primäre, sekundäre oder tertiäre Amingruppen oder eine Ethergruppe umfasst.

17. Verfahren nach Anspruch 16, bei dem die Lewis-Base ein primäres, sekundäres oder tertiäres Amin der Formel $R^1R^2R^3N$, in der R^1, R^2 und R^3 jeweils Wasserstoff, eine C_1-C_6-Alkylgruppe oder eine C_6-C_{10}-Arylgruppe, ein Polyamin, permethyliertes Polyamin, Pyridin bzw. Polypyridin darstellen oder Tetrahydrofuran ist.

18. Verfahren nach Anspruch 17, bei dem die Lewis-Base aus Dimethylamin, TMEDA $\{[(CH_3)_2NCH_2]_2\}$ und PMDETA $\{[(CH_3)_2NCH_2CH_2]_2NCH_3\}$ ausgewählt ist.

19. Verfahren nach einem der vorstehenden Ansprüche, bei dem die thermische Zersetzung gleichzeitig eine Phosphorverbindung mit mindestens einer P-P-Bindung ergibt.

20. Verfahren nach Anspruch 16, wobei die gleichzeitig erzeugte Phosphorverbindung ein cyclisches Phosphiniden ist.

21. Verfahren nach einem der vorstehenden Ansprüche, wobei der stabile heterometallische Phosphinidenkomplex umfasst:

(i) eine Vielzahl von Phosphinidenliganden, [PR], worin jedes R, die gleich oder voneinander verschieden sein können, aus C_1-C_6-Alkyl-, verzweigten Alkyl-, Cycloalkyl- oder Arylgruppen ausgewählt ist;

(ii) mindestens ein aus einem Metall der Gruppe 14 oder Gruppe 15 ausgewähltes Metall;

(iii) mindestens ein aus Li, Na, K, Rb und Cs ausgewähltes Metall der Gruppe I; und

(iv) eine Vielzahl labiler, die Lewis-Base stabilisierender Liganden, die jeweils gleich oder voneinander verschieden sein können,

und wobei das thermische Zersetzungsverfahren gleichzeitig eine cyclische Phosphinidenverbindung $[PR]_n$ ergibt, in der n 4 bis 6 ist.

22. Verfahren nach einem der vorstehenden Ansprüche, wobei der stabile heterometallische Phosphinidenkomplex umfasst:

(i) eine Vielzahl von Phosphinidenliganden, [PR], worin jedes R, die gleich oder voneinander verschieden sein können, aus C_1-C_6-Alkyl, verzweigtem Alkyl, Cycloalkyl oder Aryl ausgewählt ist;

(ii) mindestens ein aus Ge, Sn, Pb, As, Sb und Bi ausgewähltes Metall;

(iii) mindestens ein aus Li, Na, K, Rb und Cs ausgewähltes Metall;

(iv) eine Vielzahl labiler, die Lewis-Base stabilisierender Liganden, die jeweils gleich oder voneinander verschieden sein können,

und wobei das thermische Zersetzungsverfahren gleichzeitig eine cyclische Phosphinidenverbindung $[PR]_n$ ergibt, in der n 4 bis 6 ist.

23. Verfahren nach einem der vorstehenden Ansprüche, bei dem die thermische Zersetzung bei einer Temperatur von mehr als 20°C durchgeführt wird.

24. Verfahren nach Anspruch 21, bei dem die thermische Zersetzung in einem Temperaturbereich zwischen 25 und 100°C durchgeführt wird.

25. Verfahren nach einem der vorstehenden Ansprüche, bei dem sich die Phosphinidenverbindung bei der thermischen Zersetzung in Lösung in einem organischen Lösungsmittel befindet.

26. Verfahren nach einem der vorstehenden Ansprüche, bei dem das organische Lösungsmittel aus einem Kohlenwasserstoff wie n-Alkan, einem aromatischen Kohlenwasserstoff wie Toluol oder THF ausgewählt ist.

27. Verfahren nach einem der vorstehenden Ansprüche, bei dem der stabile heterometallische Phosphinidenkomplex durch die Formel $[Sb(PCy)_3]_2Li_6{\cdot}6Me_2NH$, $\{[Cyclo\text{-}(CyP)_4Sb]Na{\cdot}Me_2NH{\cdot}TMEDA\}_2$ oder $[(^tBuP)_3As{\cdot}Li{\cdot}TMEDA{\cdot}THF]$, worin Cy Cyclohexyl ist, dargestellt werden kann.

28. Verfahren nach einem der vorstehenden Ansprüche, bei dem die Zintl-Verbindung ein polymetallisches, aus Atomen eines oder mehrerer Metalle bestehendes Anion umfasst, wobei das polymetallische Anion ggfs. mit Metallkationen koordiniert sein kann und die Metallkationen mit Lewis-Base-Liganden koordiniert sind.

29. Verfahren nach Anspruch 28, bei dem die Zintl-Verbindung ein aus Atomen eines Metalls M^1 bestehendes polymetallisches Anion umfasst, wobei das polymetallische Anion ggfs. mit Kationen eines Metalls M^2 koordiniert sein kann und die Kationen eines Metalls M^2 mit Lewis-Base-Liganden Lg koordiniert sind.

30. Verfahren nach Anspruch 28, bei dem die Zintl-Verbindung die Formel $(M^1)_{n'}(M^2)_{m'}(Lg)_{p'}$ hat, wobei M^1, M^2 und Lg wie in Anspruch 29 definiert sind und n', m' und p' jeweils im Bereich von 1 bis 10 liegen.

31. Verfahren nach Anspruch 29 oder 30, bei dem M^1 ein Metall der Gruppe 13, 14 oder 15 des Periodensystems ist.

32. Verfahren nach Anspruch 29, bei dem M^1 ein Metall der Gruppe 15 des Periodensystems ist.

33. Verfahren nach Anspruch 32, bei dem M^1 aus As, Sb und Bi ausgewählt ist.

34. Verfahren nach einem der Ansprüche 29 bis 33, bei dem M^2 ein Metall der Gruppe 1 des Periodensystems ist.

35. Verfahren nach Anspruch 34, bei dem M^2 Li, Na, K oder Rb ist.

36. Verfahren nach einem der Ansprüche 30 bis 35, bei dem der Lewis-Base- Lg eine oder mehrere primäre, sekundäre oder tertiäre Amingruppen oder eine Ethergruppe umfasst.

37. Verfahren nach Anspruch 36, bei dem der Lewis-Base-Lg ein primäres, sekundäres oder tertiäres Amin der Formel $R^1R^2R^3N$, in der R^1, R^2 und R^3 jeweils Wasserstoff, eine C_1-C_6-Alkylgruppe oder eine C_6-C_{10}-Arylgruppe, ein Polyamin, permethyliertes Polyamin, Pyridin bzw. Polypyridin darstellen, oder Tetrahydrofuran ist.

38. Verfahren nach Anspruch 37, bei dem der Lewis-Base-Lg aus Dimethylamin, TMEDA $\{[(CH_3)_2NCH_2]_2\}$ und PMDETA $\{[(CH_3)_2NCH_2CH_2]_2NCH_3\}$ ausgewählt ist.

39. Verfahren nach einem der vorstehenden Ansprüche, bei dem der Phosphinidenkomplex vor der thermischen Zersetzung mit einem primären oder sekundären Amin in Kontakt gebracht wird.

40. Verfahren nach Anspruch 39, bei dem der Phosphinidenkomplex, der mit dem primären oder sekundären Amin in Kontakt gebracht wird, frei von stabilisierenden Lewis-Base-Liganden ist.

41. Verfahren nach Anspruch 39, bei dem der Phosphinidenkomplex, der mit dem primären oder sekundären Amin in Kontakt gebracht wird, einen stabilisierenden Lewis-Base-Liganden enthält, der aprotisch ist.

42. Verfahren nach einem der Ansprüche 39 bis 41, bei dem der Phosphinidenkomplex mit Dimethylamin in Kontakt gebracht wird.

43. Verfahren zur Herstellung einer intermetallischen Verbindung, umfassend

(a) die Herstellung einer Zintl-Verbindung nach einem Verfahren nach einem der vorstehenden Ansprüche, wobei die Zintl-Verbindung ein mehratomiges Anion umfasst, das aus Atomen eines Metalls M^1 besteht, wobei das mehratomige Anion ggfs. mit Kationen eines Metalls M^2 koordiniert sein kann und die Kationen eines Metalls M^2 mit stabilisierenden Liganden Lg koordiniert sind, und

(b) die anschließende Entfernung der stabilisierenden Liganden.

44. Verfahren zur Herstellung einer intermetallischen Verbindung nach Anspruch 43, bei dem die stabilisierenden Liganden Lewis-Base Liganden sind.

45. Verfahren zur Herstellung einer intermetallischen Verbindung nach Anspruch 43 oder 44, bei dem die stabilisierenden Liganden unter verringertem Druck entfernt werden.

46. Verfahren zur Herstellung einer intermetallischen Verbindung, umfassend

(a) die Herstellung einer Zintl-Verbindung, indem man einen heterometallischen Phosphinidenkomplex einer thermischen Zersetzung unterwirft, wobei die Zintl-Verbindung ein mehratomiges Anion umfasst, das aus Atomen eines Metalls M^1 besteht, wobei das mehratomige Anion ggfs. mit Kationen eines Metalls M^2 koordiniert sein kann und die Kationen eines Metalls M^2 mit stabilisierenden Liganden Lg koordiniert sind, und

(b) die anschließende Entfernung der stabilisierenden Liganden.

47. Verfahren zur Herstellung einer intermetallischen Verbindung nach Anspruch 46, bei dem der heterometallische Phosphinidenkomplex wie in einem der Ansprüche 2 bis 11 definiert ist.

48. Verfahren zur Herstellung einer intermetallischen Verbindung nach Anspruch 46 oder 47, bei dem die Zintl-Verbindung wie in einem der Ansprüche 28 bis 38 definiert ist.

49. Verfahren zur Herstellung einer intermetallischen Verbindung nach einem der Ansprüche 46 bis 48, bei dem die thermische Zersetzung bei einer Temperatur von mehr als 20°C durchgeführt wird.

50. Verfahren zur Herstellung einer intermetallischen Verbindung nach Anspruch 49, bei dem die thermische Zersetzung in einem Temperaturbereich zwischen 25 und 100°C durchgeführt wird.

51. Verfahren nach Anspruch 48 bis 50, bei dem sich die Phosphinidenverbindung bei der thermischen Zersetzung in Lösung in einem organischen Lösungsmittel befindet.

52. Verfahren nach Anspruch 51, bei dem das organische Lösungsmittel aus einem Kohlenwasserstoff wie n-Alkan, einem aromatischen Kohlenwasserstoff wie Toluol oder THF ausgewählt ist.

53. Verfahren zur Ausbildung einer intermetallischen Schicht auf einer Oberfläche, das umfasst:

(a) das Aufbringen einer Zintl-Verbindung auf die Oberfläche, wobei die Zintl-Verbindung ein mehratomiges Anion umfasst, das aus Atomen

eines Metalls M^1 besteht, wobei das mehratomige Anion mit Kationen eines Metalls M^2 koordiniert ist und die Kationen eines Metalls M^2 mit stabilisierenden Liganden Lg koordiniert sind, und

(b) die anschließende Entfernung der stabilisierenden Liganden.

54. Verfahren zur Ausbildung einer intermetallischen Schicht auf einer Oberfläche, das umfasst:

(a) das Aufbringen einer heterometallischen Phosphinidenverbindung auf die Oberfläche, wobei die heterometallische Phosphinidenverbindung wie in einem der Ansprüche 1 bis 22 definiert ist,

(b) das thermisches Zersetzen der heterometallischen Phosphinidenverbindung mit gleichzeitigem Verlust des stabilisierenden Liganden.

55. Verfahren zur Ausbildung einer intermetallischen Schicht auf einer Oberfläche, das umfasst:

(a) das Aufbringen einer heterometallischen Phosphinidenverbindung auf die Oberfläche, wobei die heterometallische Phosphinidenverbindung wie in einem der Ansprüche 1 bis 22 definiert ist,

(b) die thermische Zersetzung der heterometallischen Phosphinidenverbindung zu einer Zintl-Verbindung, wobei die Zintl-Verbindung umfasst: ein mehratomiges Anion, das aus Atomen eines Metalls M^1 besteht, und Kationen eines Metalls M^2, die mit stabilisierenden Liganden koordiniert sind, und

(b) die anschließende Entfernung der stabilisierenden Liganden.

56. Verfahren nach einem der Ansprüche 53 bis 55, bei dem die Oberfläche ein Oberflächenteil eines elektronischen Bauteils ist.

57. Verfahren zur Herstellung eines elektronischen Bauteils mit einer intermetallischen Schicht auf einem Teil seiner Oberfläche, umfassend:

(a) das Aufbringen einer Zintl-Verbindung auf die Oberfläche, wobei die Zint1-Verbindung ein mehratomiges Anion umfasst, das aus Atomen eines Metalls M^1 besteht, wobei das mehratomige Anion ggfs. mit Kationen eines Metalls M^2 koordiniert sein kann und die Kationen eines Metalls M^2 mit stabilisierenden Liganden Lg koordiniert sind, und

(b) die anschließende Entfernung der stabilisierenden Liganden.

58. Verfahren zur Herstellung einer intermetallischen Schicht auf einer Oberfläche oder einem Oberflächenteil eines elektronischen Bauteils, umfassend

(a) das Aufbringen einer heterometallischen Phosphinidenverbindung auf die Oberfläche, wobei die heterometallische Phosphinidenverbindung wie in einem der Ansprüche 1 bis 22 definiert ist,

(b) die thermische Zersetzung der heterometallischen Phosphinidenverbindung mit gleichzeitigem Verlust des stabilisierenden Liganden.

59. Verfahren zur Herstellung eines elektronischen Bauteils mit einer intermetallischen Schicht auf einem Teil seiner Oberfläche, umfassend:

(a) das Aufbringen einer heterometallischen Phosphinidenverbindung auf die Oberfläche, wobei die heterometallische Phosphinidenverbindung wie in einem der Ansprüche 1 bis 22 definiert ist;

(b) die thermische Zersetzung der heterometallischen Phosphinidenverbindung zu einer Zintl-Verbindung, wobei die Zintl-Verbindung umfasst: ein mehratomiges Anion, das aus Atomen eines Metalls M^1 besteht, und Kationen eines Metalls M^2, die mit stabilisierenden Liganden koordiniert sind, und

(b) die anschließende Entfernung der stabilisierenden Liganden.

60. Verfahren nach einem der Ansprüche 57 bis 59, bei dem die intermetallische Schicht bei der Verwendung so adaptiert ist, dass sie Elektronen aussendet.

61. Verfahren nach einem der Ansprüche 57 bis 59, bei dem das elektronische Bauteil ein photoelektrisches Bauteil ist.

62. Verwendung eines stabilen heterometallischen Phosphinidenkomplexes als Vorläufer für die Abscheidung eines intermetallischen Legierungsfilms.

63. Verwendung eines stabilen heterometallischen Phosphinidenkomplexes wie in einem der Ansprüche 2 bis 36 definiert als Vorläufer für die Abscheidung eines intermetallischen Legierungsfilms.

Revendications

1. Procédé de production d'un composé de Zintl comprenant l'exposition d'un complexe de phosphinidène hétérométallique à une décomposition thermique.

2. Procédé selon la revendication 1 où le complexe de phosphinidène hétérométallique comprend au moins deux métaux.

3. Procédé selon la revendication 2 où l'un desdits métaux est un métal du groupe 13, 14 ou 15 du tableau périodique.

4. Procédé selon la revendication 3 où l'un desdits métaux est un métal du groupe 15 du tableau périodique.

5. Procédé selon la revendication 3 où l'un desdits métaux est choisi parmi As, Sb et Bi.

6. Procédé selon la revendication 2 où l'un desdits métaux est un métal du groupe 1 du tableau périodique.

7. Procédé selon la revendication 6 où l'un desdits métaux est Li, Na, K, Rb ou Cs.

8. Procédé selon l'une quelconque des revendications précédentes où le complexe de phosphinidène hétérométallique contient un ou plusieurs ligands phosphinidènes, qui peuvent être identiques ou différents, et ayant un atome de phosphore lié de manière covalente à un groupe hydrocarboné substitué ou non substitué.

9. Procédé selon la revendication 8 où le groupe hydrocarboné substitué ou non substitué contient 1 à 15, de préférence 4 à 10 atomes de carbone.

10. Procédé selon la revendication 9 où le groupe hydrocarboné substitué ou non substitué est choisi parmi les groupes alkyle, alcényle, alcynyle, cycloalkyle, aryle, aralkyle, alkylaryle, où le substituant ou les substituants peuvent être choisis parmi les groupes fluoro et alkylsilyle en C_1-C_6.

11. Procédé selon l'une quelconque des revendications 8-10 où le complexe de phosphinidène hétérométallique contient un ou plusieurs ligands phosphinidènes ayant un atome de phosphore lié de manière covalente à un groupe cyclohexyle.

12. Procédé selon l'une quelconque des revendications précédentes où l'atome de phosphore du ou de chaque ligand phosphinidène est coordiné avec quatre atomes métalliques.

13. Procédé selon la revendication 12 où l'atome de phosphore du ou de chaque ligand phosphinidène est coordiné avec trois atomes métalliques du groupe I.

14. Procédé selon la revendication 12 ou la revendication 13 où l'atome de phosphore du ou de chaque ligand phosphinidène est coordiné avec un atome métallique du groupe 13, 14 ou 15.

15. Procédé selon l'une quelconque des revendications précédentes où le complexe de phosphinidène hétérométallique comprend un second ligand qui est une base de Lewis.

16. Procédé selon la revendication 15 où la base de Lewis comprend un ou plusieurs groupes amine primaires, secondaires ou tertiaires ou un groupe éther.

17. Procédé selon la revendication 16 où la base de Lewis est une amine primaire, secondaire ou tertiaire de formule $R^1R^2R^3N$ où R^1, R^2 et R^3 représentent chacun l'hydrogène, un groupe alkyle en C_1-C_6 ou un groupe aryle en C_6-C_{10}, une polyamine, une polyamine perméthylée, la pyridine ou la polypyridine, ou le tétrahydrofurane.

18. Procédé selon la revendication 17 où la base de Lewis est choisie parmi la diméthylamine, TMEDA $\{[(CH_3)_2NCH_2]_2\}$ et PMDETA $\{[(CH_3)_2NCH_2CH_2]_2NCH_3\}$.

19. Procédé selon l'une quelconque des revendications précédentes où la décomposition thermique conduit à la production simultanée d'un composé du phosphore ayant au moins une liaison P-P.

20. Procédé selon la revendication 16 où le composé du phosphore produit simultanément est un phosphinidène cyclique.

21. Procédé selon l'une quelconque des revendications précédentes où le complexe de phosphinidène hétérométallique stable comprend :

    (i) une pluralité de ligands phosphinidènes, [PR], où chaque R, qui peut être identique ou différent, est choisi parmi les groupes alkyle en C_1-C_6, alkyle ramifié, cycloalkyle et aryle,
    (ii) au moins un métal choisi parmi les métaux du groupe 14 ou du groupe 15 ;
    (iii) au moins un métal du groupe 1 choisi parmi Li, Na, K, Rb, Cs ; et
    (iv) une pluralité de ligands stabilisants bases de Lewis, labiles, qui peuvent être identiques ou différents,

et ledit procédé de décomposition thermique conduit à la production simultanée d'un composé de phosphinidène cyclique $[PR]_n$ où n = 4-6.

22. Procédé selon l'une quelconque des revendications précédentes où le complexe de phosphinidène hétérométallique stable comprend :

(i) une pluralité de ligands phosphinidènes, [PR], où chaque R, qui peut être identique ou différent, est choisi parmi alkyle en C_1-C_6, alkyle ramifié, cycloalkyle et aryle,
(ii) au moins un métal choisi parmi Ge, Sn, Pb, As, Sb et Bi ;
(iii) au moins un métal choisi parmi Li, Na, K, Rb et Cs ;
(iv) une pluralité de ligands stabilisants bases de Lewis, labiles, qui peuvent être identiques ou différents,

et ledit procédé de décomposition thermique conduit à la production simultanée d'un composé de phosphinidène cyclique $[PR]_n$ où n = 4-6.

23. Procédé selon l'une quelconque des revendications précédentes où la décomposition thermique est réalisée à une température supérieure à 20°C.

24. Procédé selon la revendication 21 où la décomposition thermique est réalisée dans un domaine de température de 25-100°C.

25. Procédé selon l'une quelconque des revendications précédentes où la décomposition thermique est réalisée avec le composé de phosphinidène en solution dans un solvant organique.

26. Procédé selon l'une quelconque des revendications précédentes où le solvant organique est choisi parmi un hydrocarbure comme un n-alcane, un hydrocarbure aromatique comme le toluène, ou le THF.

27. Procédé selon l'une quelconque des revendications précédentes où le complexe de phosphinidène hétérométallique stable peut être représenté par la formule $[Sb(PCy)_3]_2Li_6.6Me_2NH$, $\{[cyclo\text{-}(CyP)_4Sb]Na.Me_2NH.TMEDA\}_2$ ou $[(^tBuP)_3As.Li.TMEDA.THF]$, où Cy = cyclohexyle.

28. Procédé selon l'une quelconque des revendications précédentes où le composé de Zintl comprend un anion polymétallique consistant en atomes d'un ou plusieurs métaux, où ledit anion polymétallique peut éventuellement être coordiné avec des cations métalliques, et les cations métalliques sont coordinés avec des ligands bases de Lewis.

29. Procédé selon la revendication 28 où le composé de Zintl comprend un anion polymétallique consistant en atomes d'un métal M^1, où ledit anion polymétallique peut éventuellement être coordiné avec des cations d'un métal M^2, et les cations d'un métal M^2 sont coordinés avec des ligands bases de Lewis Lg.

30. Procédé selon la revendication 28 où le composé de Zintl a la formule $(M^1)_{n'}$ $(M^2)_{m'}$ $(Lg)_{p'}$ où M^1, M^2 et Lg sont définis comme dans la revendication 29 et n', m' et p' sont chacun dans le domaine de 1 à 10.

31. Procédé selon la revendication 29 ou la revendication 30 où M^1 est un métal du groupe 13, 14 ou 15 du tableau périodique.

32. Procédé selon la revendication 29 où M^1 est un métal du groupe 15 du tableau périodique.

33. Procédé selon la revendication 32 où M^1 est choisi parmi As, Sb et Bi.

34. Procédé selon l'une quelconque des revendications 29 à 33 où M^2 est un métal du groupe 1 du tableau périodique.

35. Procédé selon la revendication 34 où M^2 est Li, Na, K ou Rb.

36. Procédé selon l'une quelconque des revendications 30 à 35 où la base de Lewis Lg comprend un ou plusieurs groupes amine primaires, secondaires ou tertiaires ou un groupe éther.

37. Procédé selon la revendication 36 où la base de Lewis Lg est une amine primaire, secondaire ou tertiaire de formule $R^1R^2R^3N$ où R^1, R^2 et R^3 représentent chacun l'hydrogène, un groupe alkyle en C_1-C_6 ou un groupe aryle en C_6-C_{10}, une polyamine, une polyamine perméthylée, la pyridine, la polypyridine ou le tétrahydrofurane.

38. Procédé selon la revendication 37 où la base de Lewis Lg est choisie parmi la diméthylamine, TMEDA $\{[(CH_3)_2NCH_2]_2\}$ et PMDETA $\{[(CH_3)_2NCH_2CH_2]_2NCH_3\}$.

39. Procédé selon l'une quelconque des revendications précédentes où le complexe de phosphinidène est mis en contact avec une amine primaire ou secondaire avant d'être soumis à une décomposition thermique.

40. Procédé selon la revendication 39 où le complexe de phosphinidène qui est mis en contact avec la base primaire ou secondaire est exempt de ligands bases de Lewis stabilisants.

41. Procédé selon la revendication 39 où le complexe de phosphinidène qui est mis en contact avec une amine primaire ou secondaire contient un ligand base de Lewis stabilisant qui est aprotique.

42. Procédé selon l'une quelconque des revendications 39-41 où le complexe de phosphinidène est mis en contact avec la diméthylamine.

43. Procédé de production d'un composé intermétallique qui comprend :

(a) la formation d'un composé de Zintl par un procédé selon l'une quelconque des revendications précédentes, ledit composé de Zintl comprenant un anion polyatomique consistant en atomes d'un métal M^1, où ledit anion polyatomique peut éventuellement être coordiné avec des cations d'un métal M^2, et les cations d'un métal M^2 sont coordinés avec des ligands stabilisants Lg, puis
(b) le retrait des ligands stabilisants.

44. Procédé de production d'un composé intermétallique selon la revendication 43 où les ligands stabilisants sont des ligands bases de Lewis.

45. Procédé de production d'un composé intermétallique selon la revendication 43 ou la revendication 44 où les ligands stabilisants sont retirés sous pression réduite.

46. Procédé de production d'un composé intermétallique qui comprend :

(a) la formation d'un composé de Zintl par exposition d'un complexe de phosphinidène hétérométallique à une décomposition thermique, ledit composé de Zintl comprenant un anion polyatomique consistant en atomes d'un métal M^1, où ledit anion polyatomique peut éventuellement être coordiné avec des cations d'un métal M^2, et les cations d'un métal M^2 sont coordinés avec des ligands stabilisants Lg, puis
(b) le retrait des ligands stabilisants.

47. Procédé de production d'un composé intermétallique selon la revendication 46 où le complexe de phosphinidène hétérométallique est défini comme dans l'une quelconque des revendications 2-11.

48. Procédé de production d'un composé intermétallique selon la revendication 46 ou 47 où le composé de Zintl est défini comme dans l'une quelconque des revendications 28 à 38.

49. Procédé de production d'un composé intermétallique selon l'une quelconque des revendications 46 à 48 où la décomposition thermique est réalisée à une température supérieure à 20°C.

50. Procédé de production d'un composé intermétallique selon la revendication 49 où la décomposition thermique est réalisée dans un domaine de température de 25-100°C.

51. Procédé selon les revendications 48-50 où la décomposition thermique est réalisée avec le composé de phosphinidène en solution dans un solvant organique.

52. Procédé selon la revendication 51 où le solvant organique est choisi parmi un hydrocarbure comme un n-alcane, un hydrocarbure aromatique comme le toluène, et le THF.

53. Procédé de formation d'une couche intermétallique sur une surface, lequel procédé comprend :

(a) l'application d'un composé de Zintl à la surface, ledit composé de Zintl comprenant un anion polyatomique consistant en atomes d'un métal M^1, où ledit anion polyatomique est coordiné avec des cations d'un métal M^2, et les cations d'un métal M^2 sont coordinés avec des ligands stabilisants Lg, puis
(b) le retrait des ligands stabilisants.

54. Procédé de formation d'une couche intermétallique sur une surface, lequel procédé comprend :

(a) l'application d'un composé de phosphinidène hétérométallique à la surface, ledit composé de phosphinidène hétérométallique étant défini comme dans l'une quelconque des revendications 1 à 22,
(b) l'exposition du composé de phosphinidène hétérométallique à une décomposition thermique avec perte concomitante de ligand stabilisant.

55. Procédé de formation d'une couche intermétallique sur une surface, lequel procédé comprend :

(a) l'application d'un composé de phosphinidène hétérométallique à la surface, ledit composé de phosphinidène hétérométallique étant défini comme dans l'une quelconque des revendications 1 à 22,
(b) l'exposition du composé de phosphinidène hétérométallique à une décomposition thermique en un composé de Zintl, ledit composé de Zintl comprenant un anion polyatomique consistant en atomes d'un métal M^1 et un cation d'un métal M^2 qui sont coordinés avec des ligands stabilisants, puis

(c) le retrait des ligands stabilisants.

56. Procédé selon l'une quelconque des revendications 53-55 où ladite surface est une partie de surface d'un dispositif électronique.

57. Procédé de fabrication d'un dispositif électronique ayant une couche intermétallique sur une partie de surface, qui comprend :

(a) l'application d'un composé de Zintl à la surface, ledit composé de Zinti comprenant un anion polyatomique consistant en atomes d'un métal M^1, où ledit anion polyatomique peut éventuellement être coordiné avec des cations d'un métal M^2, et les cations d'un métal M^2 sont coordinés avec des ligands stabilisants, puis
(c) le retrait des ligands stabilisants.

58. Procédé de formation d'une couche intermétallique sur une surface ou partie de surface d'un dispositif électronique, lequel procédé comprend :

(a) l'application d'un composé de phosphinidène hétérométallique à la surface, ledit composé de phosphinidène hétérométallique étant défini comme dans l'une quelconque des revendications 1 à 22,
(b) l'exposition du. composé de phosphinidène hétérométallique à une décomposition thermique avec perte concomitante de ligand stabilisant.

59. Procédé de fabrication d'un dispositif électronique ayant une couche intermétallique sur une partie de surface, qui comprend :

(a) l'application d'un composé de phosphinidène hétérométallique à la surface, ledit composé de phosphinidène hétérométallique étant défini comme dans l'une quelconque des revendications 1 à 22,
(b) l'exposition du composé de phosphinidène hétérométallique à une décomposition thermique en un composé de Zintl, ledit composé de Zintl comprenant un anion polyatomique consistant en atomes d'un métal M^1 et un cation d'un métal M^2 qui sont coordinés avec des ligands stabilisants, puis
(c) le retrait des ligands stabilisants.

60. Procédé selon l'une quelconque des revendications 57-59 où la couche intermétallique est adaptée pendant l'utilisation pour jouer le rôle d'un émetteur d'électrons.

61. Procédé selon l'une quelconque des revendications 57-59 où le dispositif électronique est un dispositif photoélectrique.

62. Utilisation d'un complexe de phosphinidène hétérométallique stable comme précurseur pour le dépôt d'un film d'alliage intermétallique.

63. Utilisation d'un complexe de phosphinidène hétérométallique stable selon l'une quelconque des revendications 2 à 36 comme précurseur pour le dépôt d'un film d'alliage intermétallique.

FIG. 1

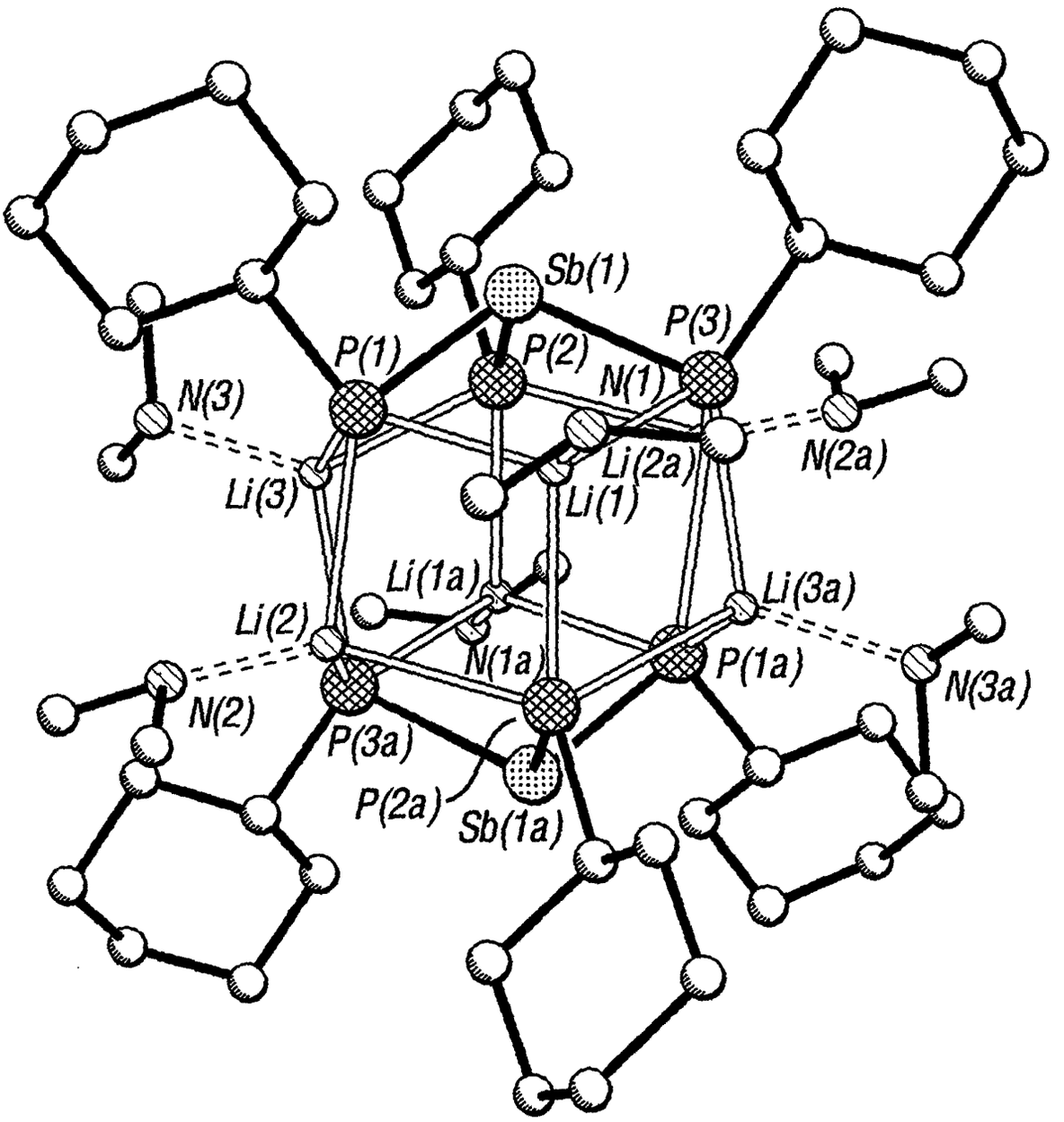

Sb(1)
P(1)
P(2)
P(3)
N(1)
N(3)
Li(3)
Li(2a)
N(2a)
Li(1)
Li(1a)
Li(3a)
Li(2)
N(1a)
P(1a)
N(3a)
N(2)
P(3a)
P(2a)
Sb(1a)

FIG. 2

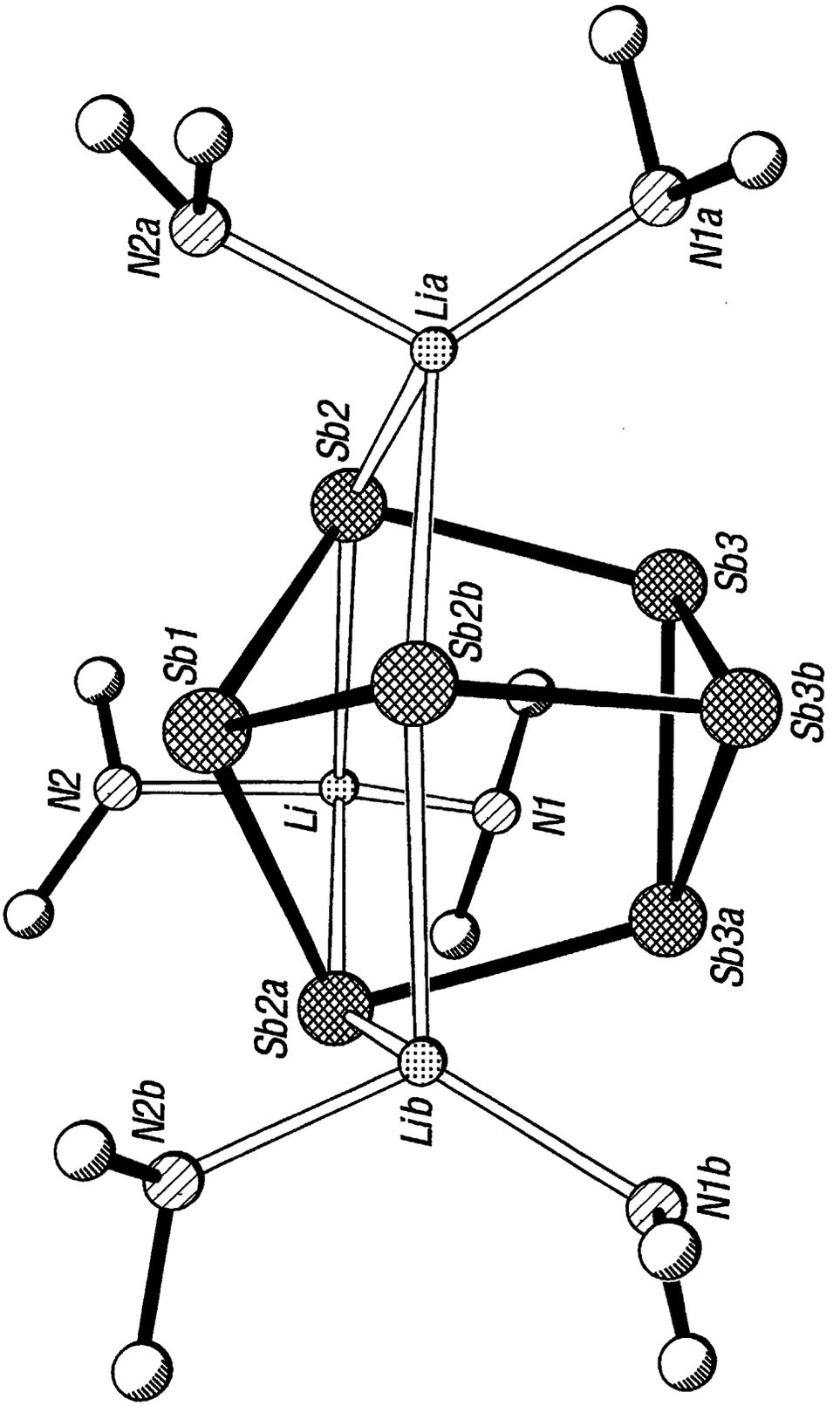


FIG. 3

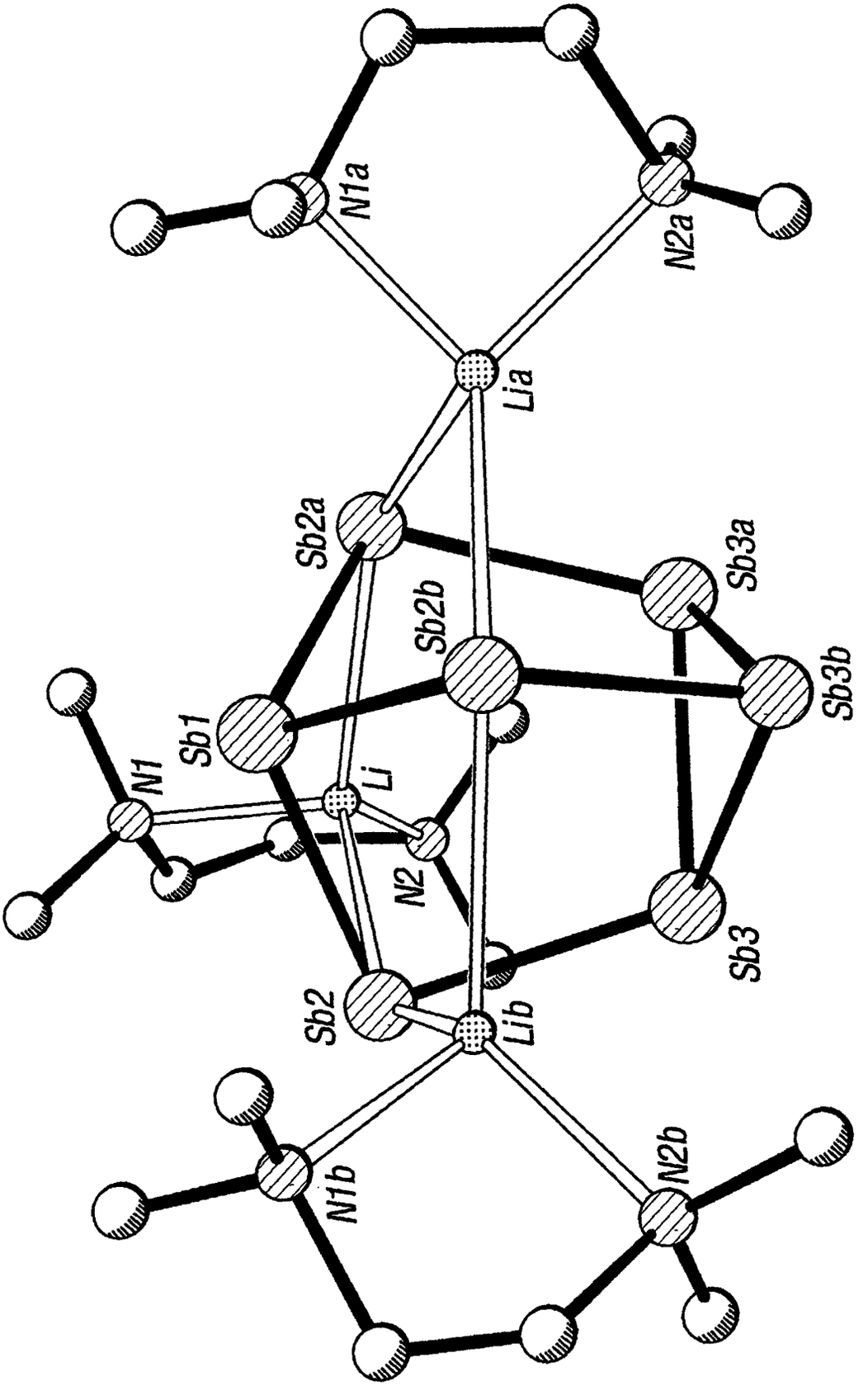


FIG. 4

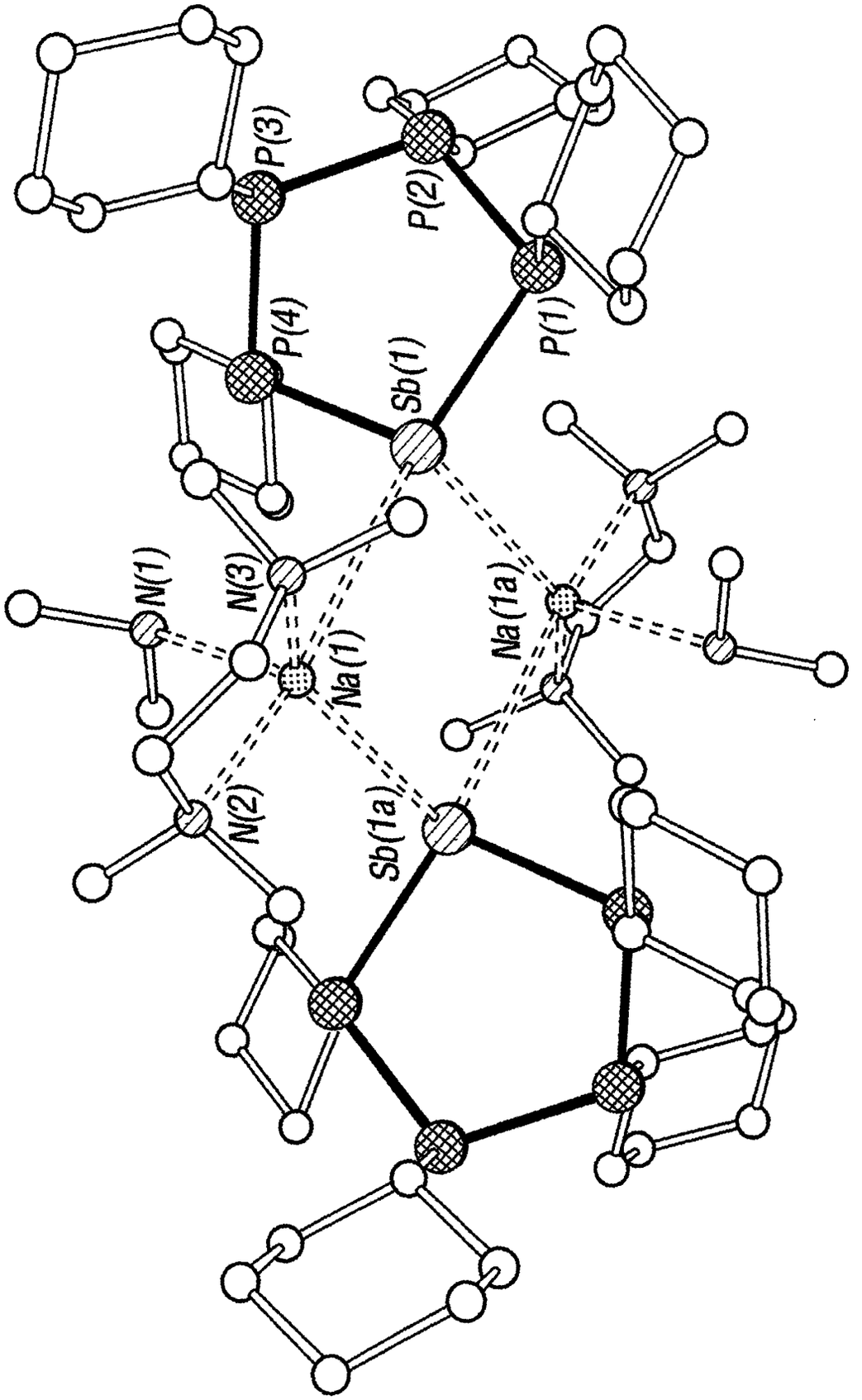
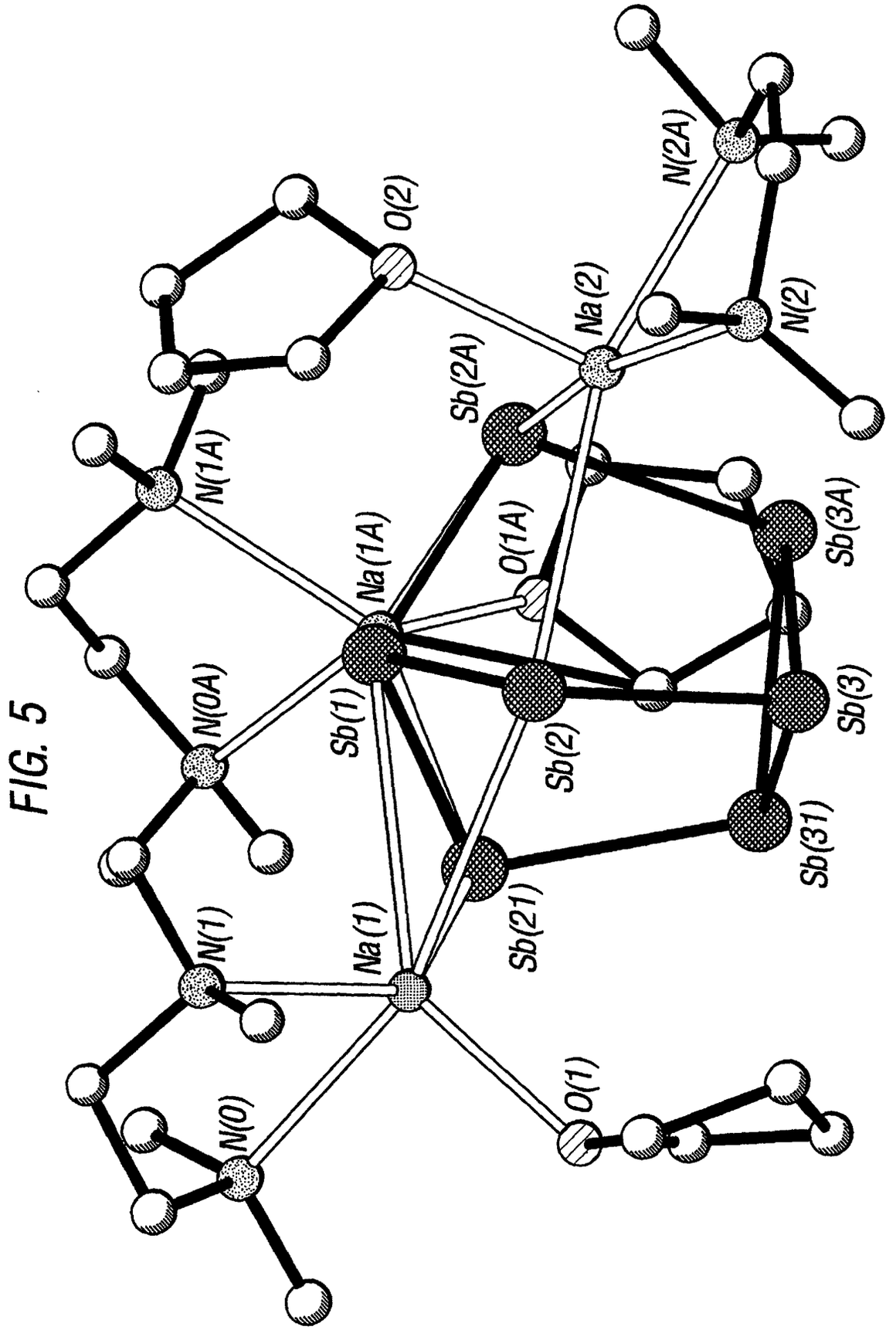


FIG. 5


O(2)
N(2A)
Na(2)
N(2)
Sb(2A)
N(1A)
Na(1A)
O(1A)
Sb(3A)
N(0A)
Sb(1)
Sb(2)
Sb(3)
Sb(31)
Sb(21)
N(1)
Na(1)
O(1)
N(0)

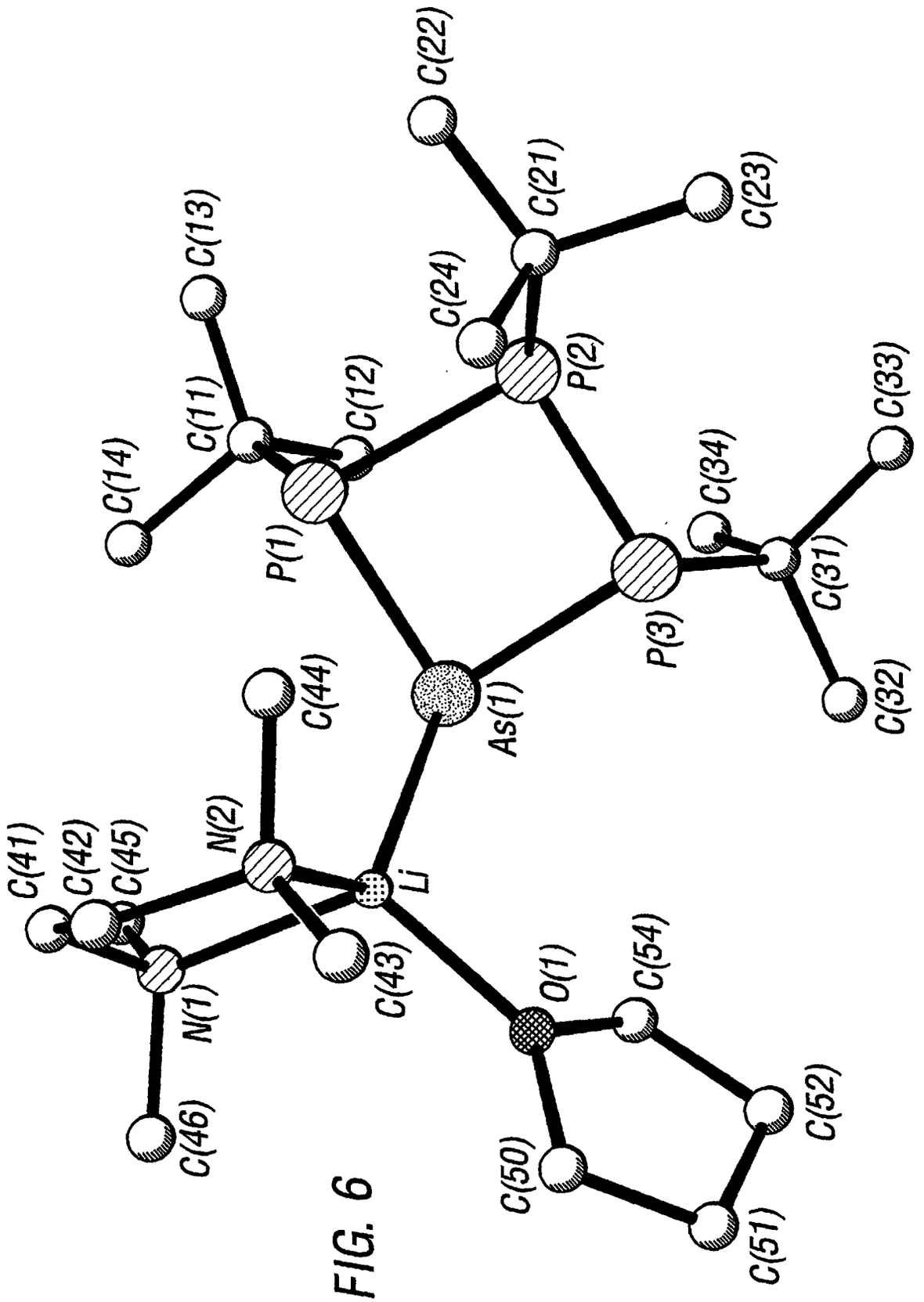

C(22)
C(21)
C(23)
C(24)
P(2)
C(13)
C(11)
C(12)
C(14)
P(1)
C(33)
C(34)
C(31)
P(3)
C(32)
C(44)
As(1)
C(41)
C(42)
C(45)
N(2)
Li
C(43)
O(1)
C(54)
N(1)
C(46)
C(50)
C(52)
C(51)

FIG. 6

FIG. 7

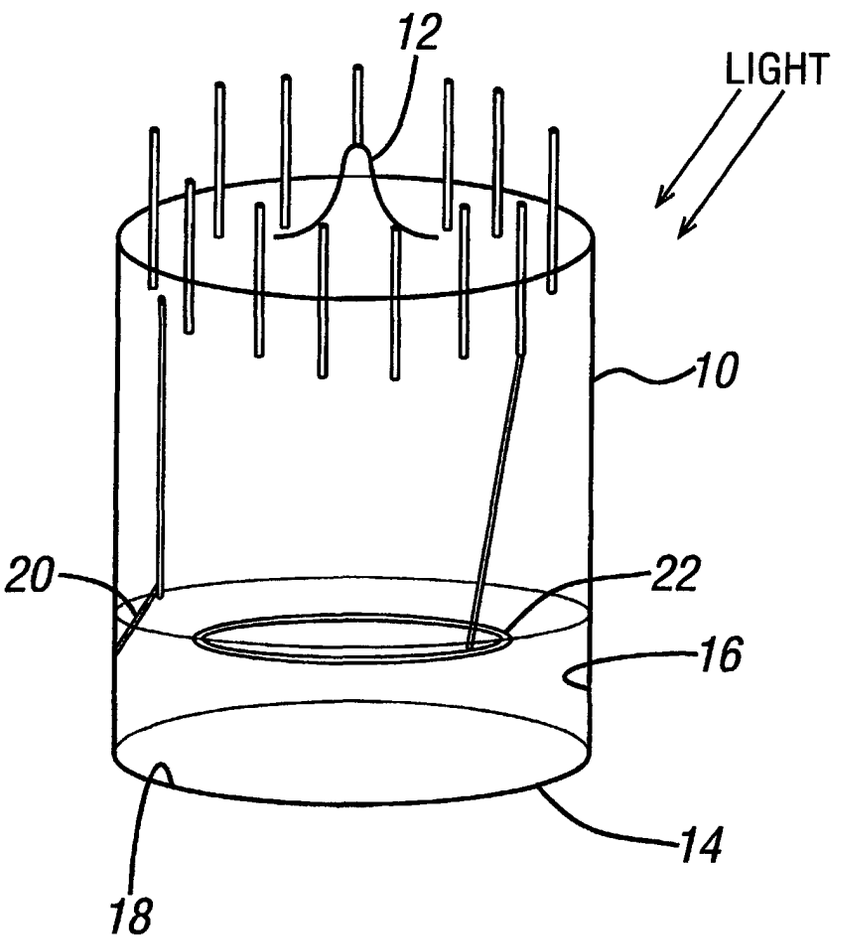
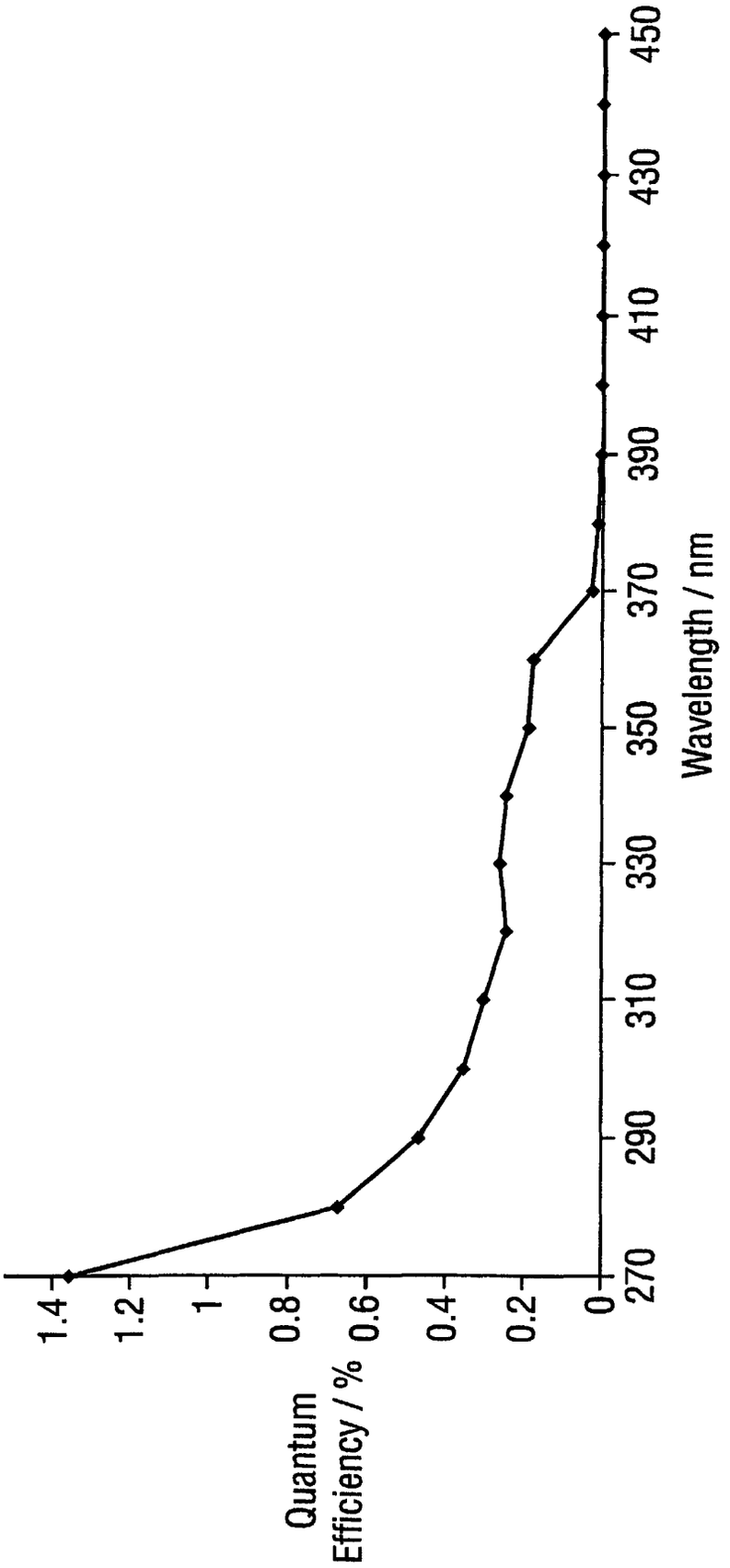


FIG. 8


Quantum Efficiency / %
1.4
1.2
1
0.8
0.6
0.4
0.2
0
270
290
310
330
350
370
390
410
430
450
Wavelength / nm